U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-283 697

Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry

Environmental Science and Engineering, Inc., Gainesville, Fla

Prepared for

Industrial Environmental Research Lab., Research Triangle Park, N.C.

Jun 78

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-78-124
June 1978

Research and Development

PB 283 697

EPA

Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-124	2.	3. RECIPIENT'S ACCESSION NO. PB283697

4. TITLE AND SUBTITLE Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry

5. REPORT DATE June 1978

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) A.A. Linero and R.A. Baker

8. PERFORMING ORGANIZATION REPORT NO

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Science and Engineering, Inc.
P.O. Box 13454
Gainesville, Florida 32604

10. PROGRAM ELEMENT NO. 1AB604

11. CONTRACT/GRANT NO. 68-02-1330, Task 3

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED Task; 12/73-1/75

14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer Edward L. Wooldridge is no longer with EPA. For details contact R.A. Venezia, Mail Drop 62, 919/541-2547.

16. ABSTRACT The report gives results of a study of gaseous emissions from gypsum disposal and cooling water ponds to determine their potential as sources of airborne fluorides from the manufacture of phosphoric acid. A model of the chemistry within the pond environment was developed. Previous emission rate studies were evaluated with respect to assumptions, methodologies, and conclusions: none provided a sufficient basis for determining a fluoride emission factor. The ponds, found in major phosphate production areas (e.g., Florida, North Carolina, and the Western U.S.), usually cover several hundred acres. Process water enters a pond at over 100 F, and leaves at lower temperatures after evaporative cooling. Ambient concentrations near a typical pond were calculated by predictive modeling methods, assuming emission rates of 0.1, 1, and 10 lb per acre per day. At the higher rates, control of fluoride emissions appears necessary, based on TLV criteria adjusted for the general population. An analysis of possible control methods indicated that liming is too expensive an alternative. Capital costs are too high for the complete Kidde process. The most promising method appears to be the Swift process for fluorosilicic acid recovery, coupled with segregation of the cooling and gypsum pond waters. The hemi/dihydrate process also appears to be promising.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Calcium Oxides	Pollution Control	13B
Gypsum		Stationary Sources	08G
Ponds		Gypsum Ponds	08H
Phosphoric Acids		Liming	07B
Industrial Processes		Fluorosilicic Acid	13H
Fluorides		Kidde Process	
Mathematical Models		Swift Process	12A

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 230
	20. SECURITY CLASS (This page) Unclassified	22. PRICE PC A11 MF A01

EPA Form 2220-1 (9-73)

EPA-600/2-78-124
June 1978

Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry

by

A.A. Linero and R.A. Baker

Environmental Science and Engineering, Inc.
P.O. Box 13454
Gainesville, Florida 32604

Contract No. 68-02-1330
Task No. 3
Program Element No. 1AB604

EPA Project Officer: Edward L. Wooldridge

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

TABLE OF CONTENTS

Page No.

Figures v

Tables viii

1.0 Industry Description 1

  1.1 Process Description - Role of the gypsum pond 1

  1.2 Size and Trends of the Phosphoric Acid Manufacturing Industry 4

  1.3 Distribution of Gypsum Ponds 6

2.0 The Role of the Gypsum Pond in an Integrated Phosphoric Acid/Fertilizer Complex 12

  2.1 Process Description 14

  2.2 Characterization of Sources of Gypsum Pond Fluorides 49

  2.3 Section 2 Conclusions 59

3.0 Gypsum Pond Chemistry 61

  3.1 Source of Fluorine in Gypsum Ponds 61

  3.2 Chemical Environment Within the Gypsum Pond 64

  3.3 Development of a Model 68

  3.4 Discussion of the Simplified Gypsum Pond Model. . . . 78

  3.5 Section 3 Conclusions 79

4.0 Determination of Fluoride Emission Factor 81

  4.1 Review of Cross and Ross' Study 81

  4.2 Review of Tatera's Study 88

  4.3 Review of King's Study 97

  4.4 Comparison of Emission Factors from the Literature 139

Page No.

5.0 Determination of Gaseous Fluoride Concentrations in the Vicinity of a Gypsum Pond 143

5.1 Description of a Typical Gypsum Pond 143

5.2 Ground Level Gaseous Fluoride Concentrations in the Vicinity of a Gypsum Pond 146

5.3 Computer Model Sensitivity Analysis 150

6.0 Identification of Control Techniques 153

6.1 Kidde Process 161

6.2 Swift Process 171

6.3 Liming of Cooling Ponds 179

6.4 Gypsum Transport by Conveyor Belt 189

6.5 Pretreatment of Ore by Calcining 191

6.6 Hemi/Dihydrate Process 193

7.0 Demonstration Costs 201

7.1 Verification of Predicted Fluoride Emission 201

7.2 Verification of the Swift Vapor Absorbtion System . . 209

Bibliography 216

LIST OF FIGURES

Page No.

1.1 Wet Process for Production of Phosphoric Acid 2

1.2 Approximate Location of Major Wet Phosphoric Acid Production Facilities 8

1.3 Approximate Locations of Gypsum Ponds in Central Florida 9

1.4 Map Showing General Land Ownership Around Gypsum Ponds in the Mulberry Area of Central Florida 10

1.5 Map Showing General Land Ownership Around Gypsum Ponds in Bartow-Fort Meade Area of Central Florida 11

2.1 Phase Equilibrium Diagram for $CaSo_4$-P_2O_5-H_2O System (Dalgran, p. 94) 20

2.2 Typical Dihydrate Process with Vacuum Acid Concentration and Fluosilicic Acid Recovery 22

2.3 Hemihydrate-dihydrate Phosphoric Acid Process (Takeuchi, p. 303) 22

2.4 Defluorinated Phosphoric Acid - Vacuum Process (EPA 440/1-53/043) 30

2.5 Defluorinated Phosphoric Acid - Submerged Combustion (EPA 440/1-75/043) 30

2.6 Defluorinated Phosphoric Acid - Aeration Process (EPA 440/1-75/043) 31

2.7 Normal Superphosphate and Triple Superphosphate - Run-of-Pile Process Schematic (Shrieve, p. 271) 40

2.8 Granulated Triple Superphosphate (EPA 440/1-74-011-a) . . . 41

2.9 Diammonium Phosphate Process Schematic (Shrieve, p. 227) . . 44

2.10 Defluorinated Phosphate Rock - Fluid Bed Process Schematic (EPA 440/1-74/043) 46

2.11 Phosphate Fertilizer Complex - Fluoride and Water Balance 58

3.1 Titration of Gypsum Pond Water with 1 N NaOH 66

Page No.

3.2 Buffer Capacity of Gypsum Pond Water 67

3.3 Graphic Initial Description of Some Pertinent Gypsum Pond Reactions 69

3.4 Species Predominance Diagram for 0.4 M HF Solution 71

3.5 Effect of Liming on Fluoride Evolution from Gypsum Pond Water (HEW, 1970) 72

3.6 Major Gypsum Pond Equilibrium 77

4.1 Location of A-Frame on Gypsum Pond 83

4.2 Dimensions of A-Frame Used by Cross 84

4.3 Drawing of Model Gypsum Pond and Water Bath Used in Gypsum Pond Studies 92

4.4 Schematic Diagram of Experimental Set-up Used in Gypsum Pond Studies 93

4.5 Tatera's Emission Factors for Process Water at 75°, 85°, 95°F. 95

4.6 Tangential Flow Along a Sharp-Edge Semi-Infinite Flat Plate With Mass Transfer Into Stream 103

4.7 Fluorine Vapor Pressure Over Pond Water 113

4.8 Fluoride Emission Rates for Ponds with Water Containing 0.335 g moles/liter Fluorides, V = Wind Speed at 16 Meters in Meters Per Second 117

4.9 Fluoride Emission Rates for Ponds with Water Containing 0.628 g moles/liter Fluorides, V_{16} + Wind Speed at 16 Meters in Meters Per Second 118

4.10 Line Source Simulation of a Rectangular Area Source 123

4.11 Ambient Air Sampler Used in King's Study 125

4.12 Pond 10 Plot Sketch 128

4.13 Pond 20 Plot Sketch 131

4.14 Pond 10 - Measured Vs. Calculated Ambient Air Concentrations at Samplers 136

Page No.

4.15 Pond 20 - Measured Vs. Calculated Ambient Air Concentrations at Samplers 137

5.1 Typical Gypsum Pond Servicing a 1,000 TPD P_2O_5 Plant 145

5.2 Isopleths of Calculated Ground-Level Fluoride X/Q Ratios Downwind of a Hypothetical Gypsum Pond 149

5.3 Isopleths of Calculated Ground-Level Fluoride X/Q Ratios Downwind of a Hypothetical Gypsum Pond 150

6.1 Two Pond System for Phosphoric Acid Plant 157

6.2 Kidde Closed-Loop Fluorine Recovery for a 1,000 TPD P_2O_5 Plant 163

6.3 Kidde Process for Recovery of AlF_3 from Waste $(NH_4)_2SiF_6$ 171

6.4 Swift Process for Fluorine Recovery at a 1,000 TPD P_2O_5 Plant 173

6.5 Fluoride Vapor Pressure Vs. pH 182

6.6 Proposed Single Liming System 184

6.7 Hemi/Dihydrate Wet Process for Phosphoric Acid Manufacture 198

7.1 Theoretical Ambient Concentration Profile as a Function of Height 205

7.2 Ambient and Pond Emission Sampling Network - Aerial View 209

LIST OF TABLES

Page No.

1.1 North American Consumption of Phosphoric Acid 5

2.1 Integration of Production in the Fertilizer Industry (EPA-440/1-74-011-a) 13

2.2 Typical Composition and Particle Size of Commercial Grades of Florida Phosphate Rock (Legal, p. 21) 16

2.3 Composition of Filtered Wet-Process Phosphoric Acids (Slack, p. 656) 18

2.4 Effect of Concentration on Compostion of Wet-Process Phosphoric Acids (Legal, p. 47) 35

2.5 Analyses of Wet-Process Acids and of Solids Obtained by Filtering the Acids (Hein, p. 695) 35

2.6 Fluoride Content of Phosphate Rock (Teller, p. 745) 50

2.7 Distribution of Fluoride in Dihydrate Process 51

2.8 Fluoride Distribution in Phosphoric Acid Production (Sanders, p. 765) 53

2.9 Fluoride Distribution in Phosphoric Acid Production (Fox) . 55

2.10 Distribution of Fluorides from Florida Phosphate Rock (Huffstutler, p. 728) 55

2.11 Phosphate Complex Water Usage (EPA 440/1-74-011-a) 56

2.12 Water Requirements for Phosphoric Acid Production (Lutz, p. 195) 57

3.1 Major Cation and Anion Concentrations in Gypsum Pond Water. After ESE, 1974 62

3.2 Formation Constants of Al and Fe Fluoride Species 74

[illegible].1 Results of Cross and Ross' Greenhouse Experiment on a Gypsum Pond 87

4.2 Analysis of Variance for King's Vapor Pressure Data 115

4.3 Measured Background Ambient Fluoride Concentrations and Simulation Model Estimates 134

Page No.

4.4 Comparison of Emission Factors Predicted by King and Tatera at Various Temperatures 142

5.1 Sensitivity Analysis for the Finite Line Source Model 153

6.1 Capital Investment and Operating Costs for Fluoride Control of a 1000 TPD P_2O_5 Plant 159

6.2 Capital Investment Requirements for Kidde Process Producing 29,000 TPY $(NH_4)_2SiF_6$ (1,000 TPD P_2O_5) 168

6.3 Annualized Operating Costs for Kidde Process 169

6.4 Fluorine Material Balance in a 1,000 TPD P_2O_5 Plant Utilizing the Swift Vapor Absorption Process 176

6.5 Capital Investment Requirements for the Swift Vapor Absorption System 177

6.6 Annualized Operating Costs for Swift Process 179

6.7 Effect of Liming on Fluoride Evolution From Gypsum-Pond Water 181

6.8 Fluorine Material Balance in a 1,000 TPD P_2O_5 Plant Utilizing Liming as Fluoride Control Strategy 185

6.9 Capital Investment Requirements for Single Liming System 188

6.10 Annualized Operating Costs for Single Liming 189

6.11 Capital Investment Requirements for Dry Gypsum Conveyor . . . 191

6.12 Capital Investment Requirements for Pre-Calcining of Phosphate Ores 195

6.13 Comparative Process Economics 201

7.1 Cost Breakdown for Fluoride Emission Determination from Two Cooling Ponds 211

7.2 Pilot Plant Program Costs for the Swift Vapor Absorbtion System 213

7.3 Estimated Costs for Demonstration of Swift Process at a 500 TPD - P_2O_5 Facility 216

1.0 INDUSTRY DESCRIPTION

Phosphoric acid is the basic building block from which essentially all mixed fertilizer used in the United States is manufactured. Over 75% of this acid is manufactured by the wet process method. This consists of digestion of phosphate rock with a strong acid, such as sulfuric or nitric acid, to convert the phosphate from practically water insoluble to a water soluble form. The acid used in this process is selected on the basis of several factors including cost, simplicity of the process, materials of construction and desired end products. In the United States, sulfuric acid is used in nearly 99% of the total U.S. production of phosphoric acid by the wet process. Nitric acid accounts for almost all of the remainder.

1.1 PROCESS DESCRIPTION - ROLE OF THE GYPSUM POND

The raw materials used in the sulfuric acid acidulation of phosphate rock are ground phosphate rock, 93% sulfuric acid, and water. Phosphate rock is mixed with the sulfuric acid after the acid has first been diluted with water to a 55-70% H_2SO_4 concentration. As shown in Figure 1.1, this mixing takes place in an attack vessel. This vessel is of sufficient size to hold the raw materials mixture for several hours. The simplified overall chemical reaction is represented by:

$$3\ Ca_3\ (PO_4)_2\ (S) + 9\ H_2SO_4\ (1) + 18\ H_2O\ (1) \rightarrow 6\ H_3PO_4\ (1) + 9\ CaSO_4 \cdot 2\ H_2O\ (S)$$

In reality, phosphate rock is not the pure compound indicated, but rather a fluorapitite material containing minor quantities of fluorine, iron,

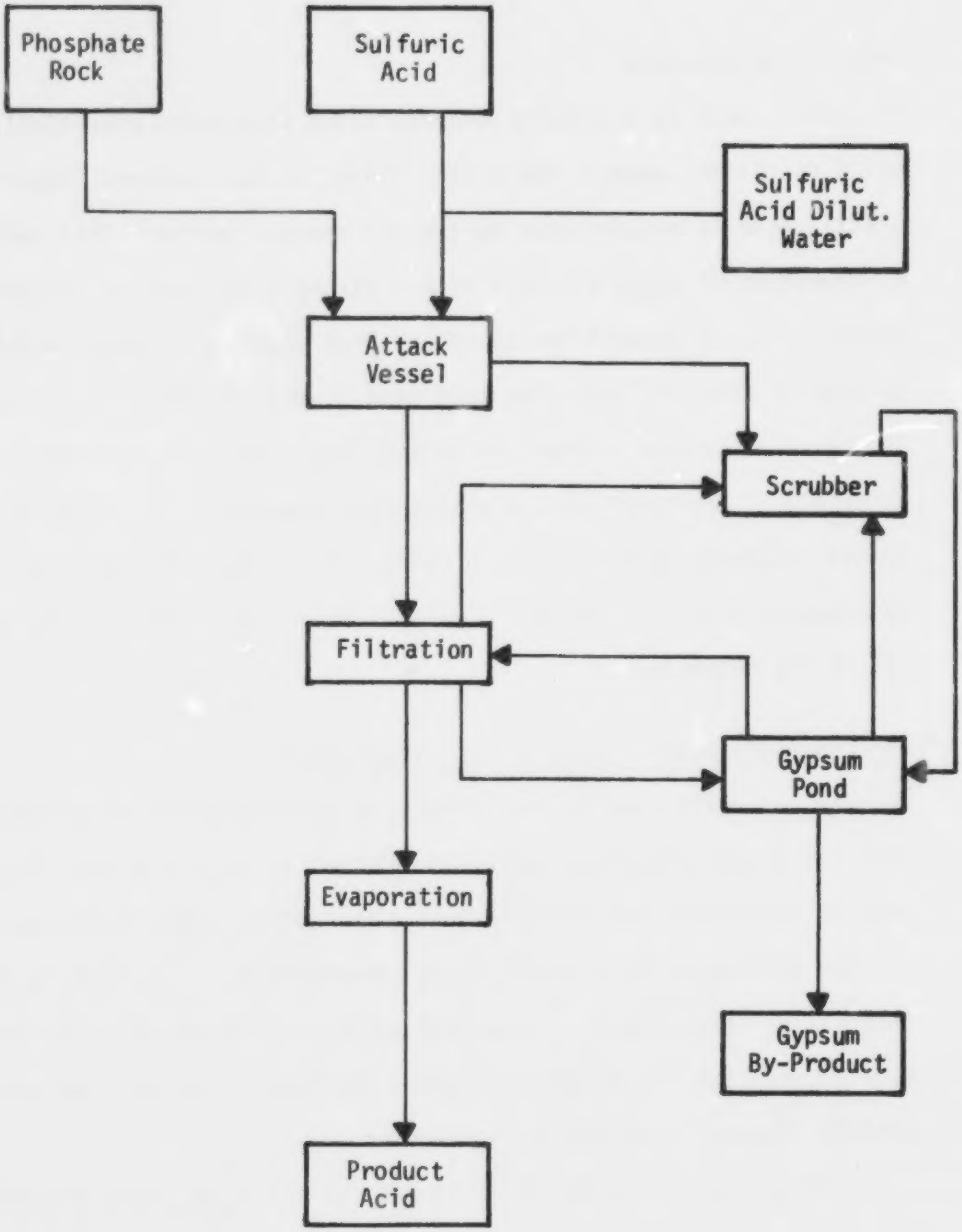


Figure 1.1 Wet Process for Production of Phosphoric Acid.

aluminum, silica and uranium. Of these the one presenting the most serious overall process problem is fluorine.

Fluorine is evolved from the attack vessel and other plant equipment as either the gas silicon tetrafluoride or hydrofluoric acid. Both of these gases can be collected in a wet scrubber unit. Additional fluorine remains in the by-product gypsum ($CaSO_4$) in a variety of fluorine compounds.

Following the reaction in the digestor, the mixture of phosphoric acid and gypsum is pumped to a filter which mechanically separates the solid gypsum from the phosphoric acid. The magnitude of the by-product gypsum is best appreciated by the fact that the production of each pound of pure phosphoric acid creates approximately 2.5 pounds of gypsum. The gypsum is generally sluiced with contaminated water from the plant to a gypsum pond. The phosphoric acid separated from the gypsum is collected for further processing.

The gypsum pond is an impoundment of from 65 to 670 hectares (160 to 1400 acres) in area. This impoundment serves two functions. One function is as a storage area for waste by-product gypsum. The second is as an area for atmospheric evaporative cooling of the contaminated water prior to its reuse in the various process units. This pond system functions in a closed loop mode most of the time, releasing water for treatment only during heavy rainfall.

1.2 SIZE AND TRENDS OF THE PHOSPHORIC ACID MANUFACTURING INDUSTRY

The manufacture of phosphoric acid is basic to the phosphate fertilizer industry. The past and predicted North American consumption of phosphoric acid is outlined in Table 1.1.

In the early 1960's, large wet process phosphoric acid plants were in the 200-300 tons P_2O_5 per day range, with multiple pieces of equipment required to perform single unit operations such as acidulation and filtration. By 1965, single train phosphoric acid units and single unit operations equipment with capacities of 500 tons P_2O_5 per day became commonplace, followed with 900 tons per day plant in 1967. Several plants now being designed and constructed have capacities of 1000-1200 tons P_2O_5 per day.

Currently there are about 40 wet process phosphoric acid plants operating in 15 states with capacities ranging from 45,000 to 440,000 tons P_2O_5 per year. The largest plants, which account for more than 50% of the nation's capacity are located near the phosphate rock sources in Florida. There are a few located along the Gulf Coast and the Mississippi River and isolated plants in North Carolina, Idaho, Utah, and California. The North Carolina, Idaho, and Utah plants utilize locally mined rather than Florida mined phosphate rock.

The construction of gypsum ponds is generally in proportion to the number and size of new plants constructed. However, new gypsum ponds may not be built in the future if the economics of the electric furnace process become competitive with those of the wet process. In this

TABLE 1.1

NORTH AMERICAN CONSUMPTION OF PHOSPHORIC ACID

YEAR	CONSUMPTION (Millions of Metric Tons) as H_3PO_4
1965	5.0
1970	6.9
1975 (est)	8.7
1980 (est)	11.0

'65 - '70 Growth Rate = 7%

'70 - '80 Growth Rate = 5%

process, the phosphate rock is reduced to phosphorus by the furnace and is subsequently converted to phosphoric acid. This eliminates the use of sulfuric acid in the process and the need for gypsum ponds. The major factor in the economics of this process is the cost of electricity. The Florida phosphate companies have been negotiating with the power companies for lower rates in anticipation of expanding the electric furnace production. If these new production methods can be employed, the industry will go through a technological revolution.

1.3 DISTRIBUTION OF GYPSUM PONDS

Gypsum ponds are an important part of the wet phosphoric acid process. They are generally diked areas where the gypsum by-product can settle out and the surplus water is collected for reuse. Approximately one acre foot of disposal volume is required per year for each daily ton of P_2O_5 produced by the plant.

The location of gypsum ponds thus depends upon the location of wet phosphoric acid plants. These plants are generally located either near the phosphate rock mine or near areas of large fertilizer use with inexpensive bulk transporation facilities. Thus the plants are located near mines in central and northern Florida; North Carolina; Idaho; and Utah; near the coastal ports of Wilmington, Delaware; Pascagoula, Mississippi; Houston, Texas; and New Orleans, Louisiana; along the Mississippi River and its tributaries at St. Paul, Minnesota; St. Louis, Missouri; Helena, Arkansas; Chicago, Illinois; Gary, Indiana; Tulsa, Okalhoma; Joplin, Missouri; and several places in central Illinois;

and along railroad routes from the western mines to central and southern California. These locations are shown generally in Figure 1.2.

Generally, the ponds associated with the non-mining locations are in heavy industry sections of cities, and as such are generally surrounded by other heavy industries or transportation complexes. The mining locations are usually more remote from centers of population, but the worst case situation is in central Florida.

The Florida plants account for well over half the United States capacity for producing phosphoric acid by the wet process; thus the majority of gypsum ponds may be found there. A more detailed map of the Polk-Hillsborough County area of Florida, shown in Figure 1.3 reveals the location of several gypsum ponds. These are generally some distance from the centers of population; but because of the population growth in these areas some ponds are rather close. Typically, these ponds are surrounded by land held by various members of the phosphate industry. Where not being mined, the land is used as raw pasture for cattle, with some citrus groves. In most cases, the land can be classified as high scrub land or low river swamp area.

In mined out areas there are recreation facilities, citrus groves and improved pasture, as well as some housing in the most desirable areas. A general land ownership map is shown in Figures 1.4 and 1.5. The average population density in the areas outside the cities of Bartow and Fort Meade is approximately 0.14* people per acre. The overall population density for Polk County is 0.23* people per acre.

---

*est. July 1, 1974 based on 1970 census.

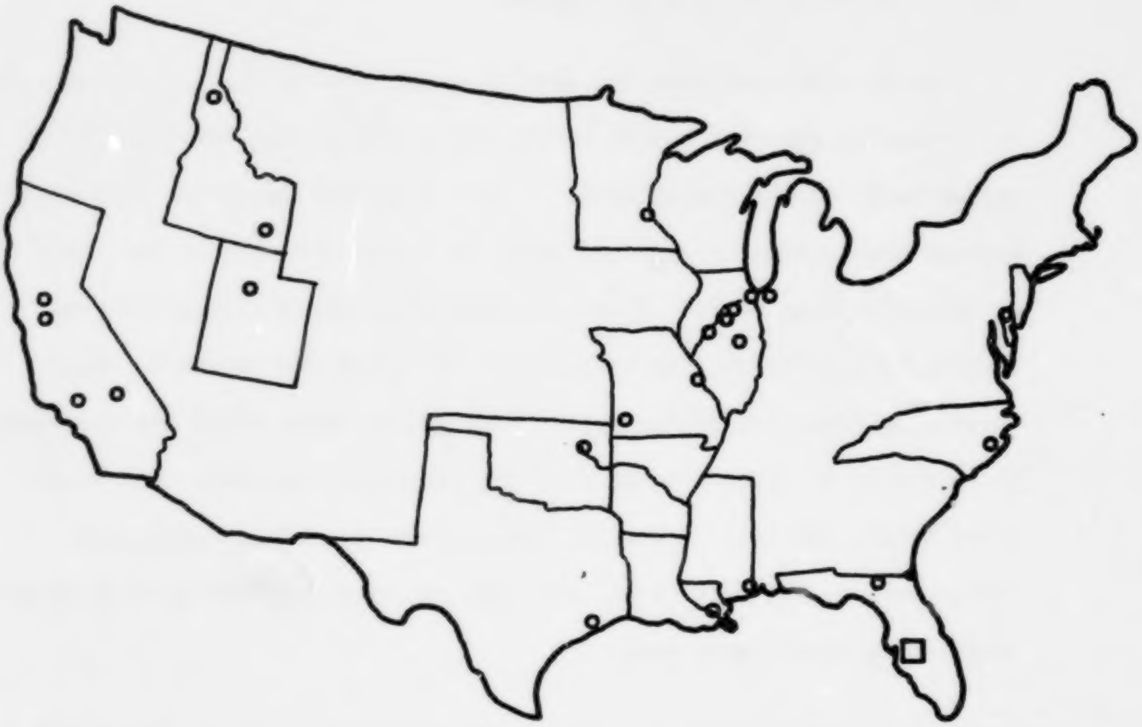


Figure 1.2. Approximate Location of Major Wet Phosphoric Acid Production Facilities.

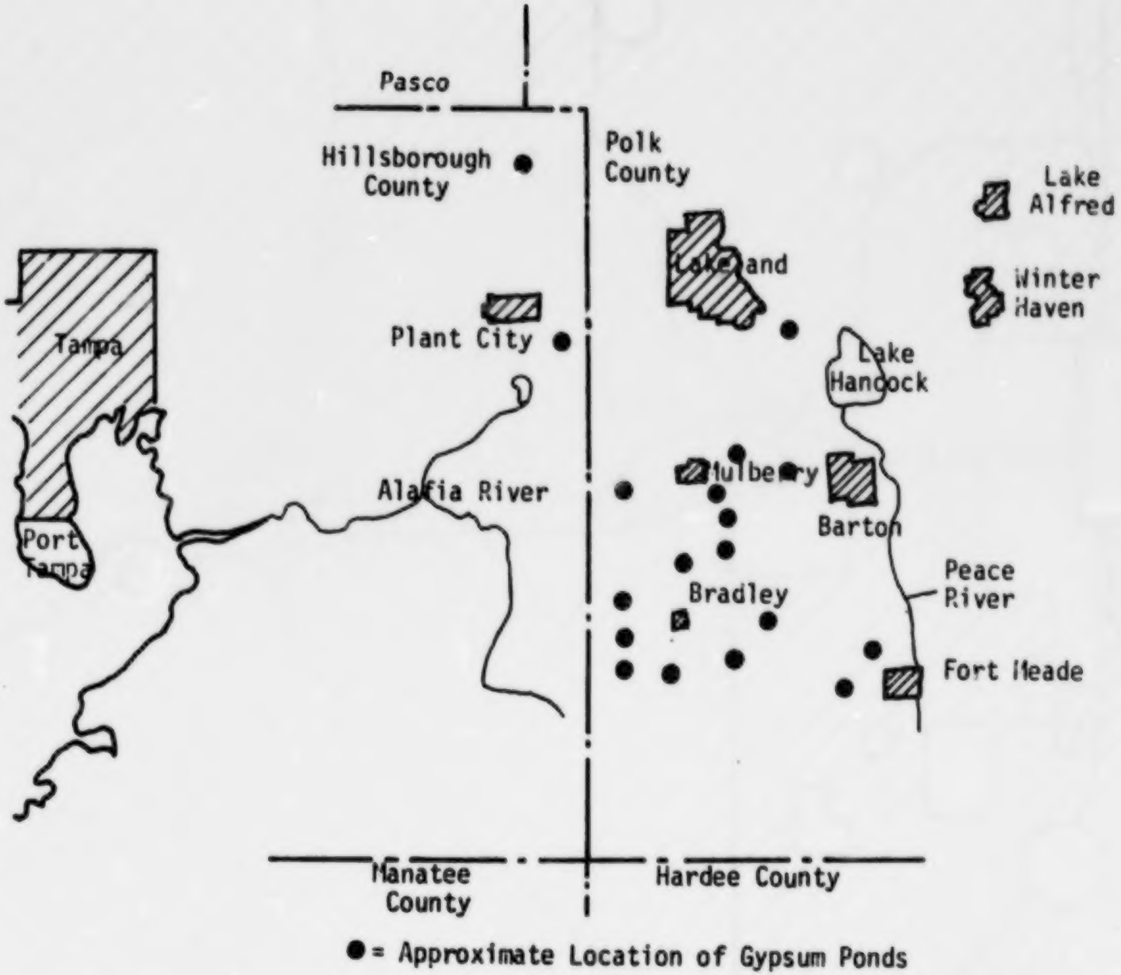
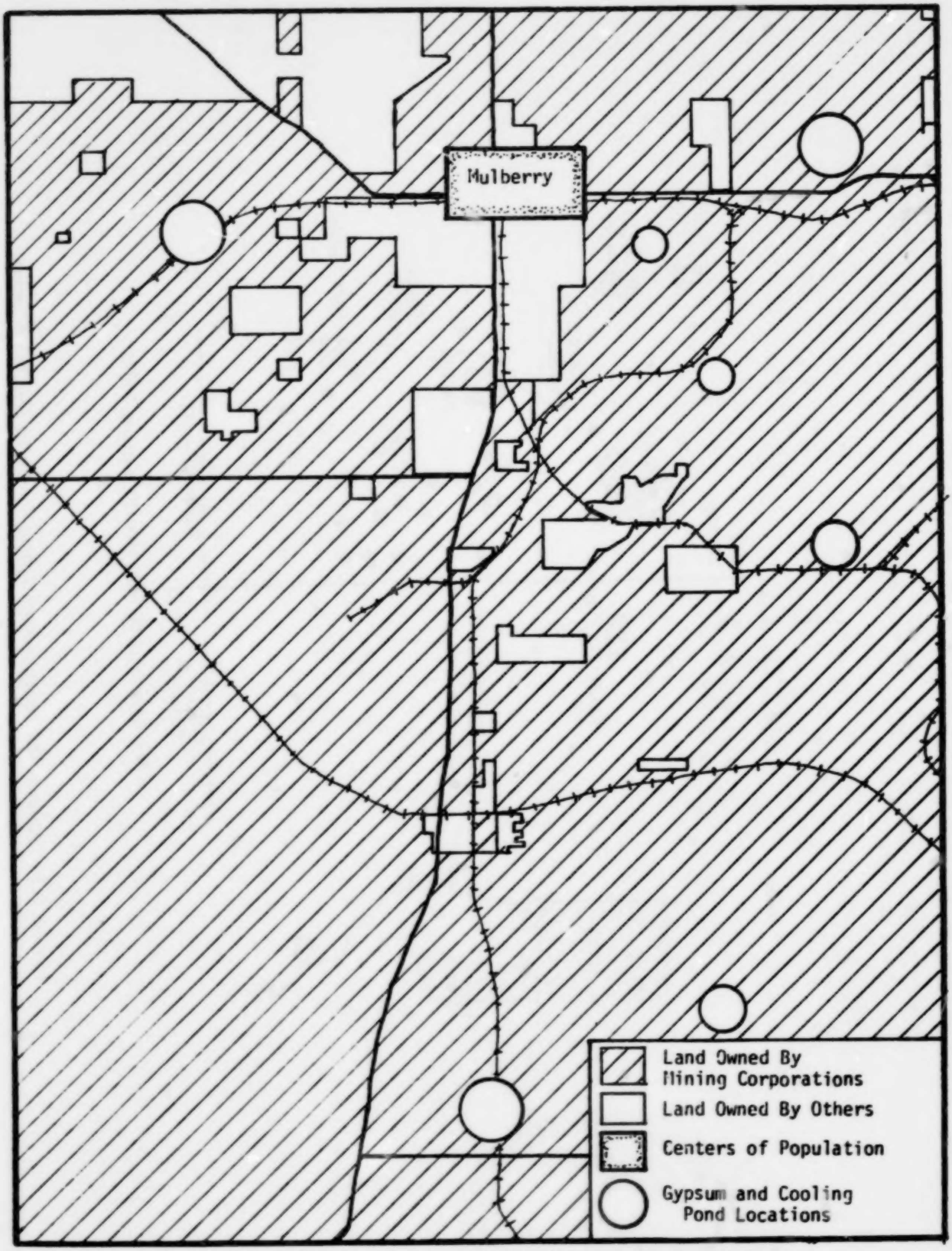


Figure 1.3. Approximate Locations of Gypsum Ponds in Central Florida.



Mulberry
Land Owned By Mining Corporations
Land Owned By Others
Centers of Population
Gypsum and Cooling Pond Locations

Figure 1.4 Map Showing General Land Ownership Around Gypsum Ponds in the Mulberry Area of Central Florida.

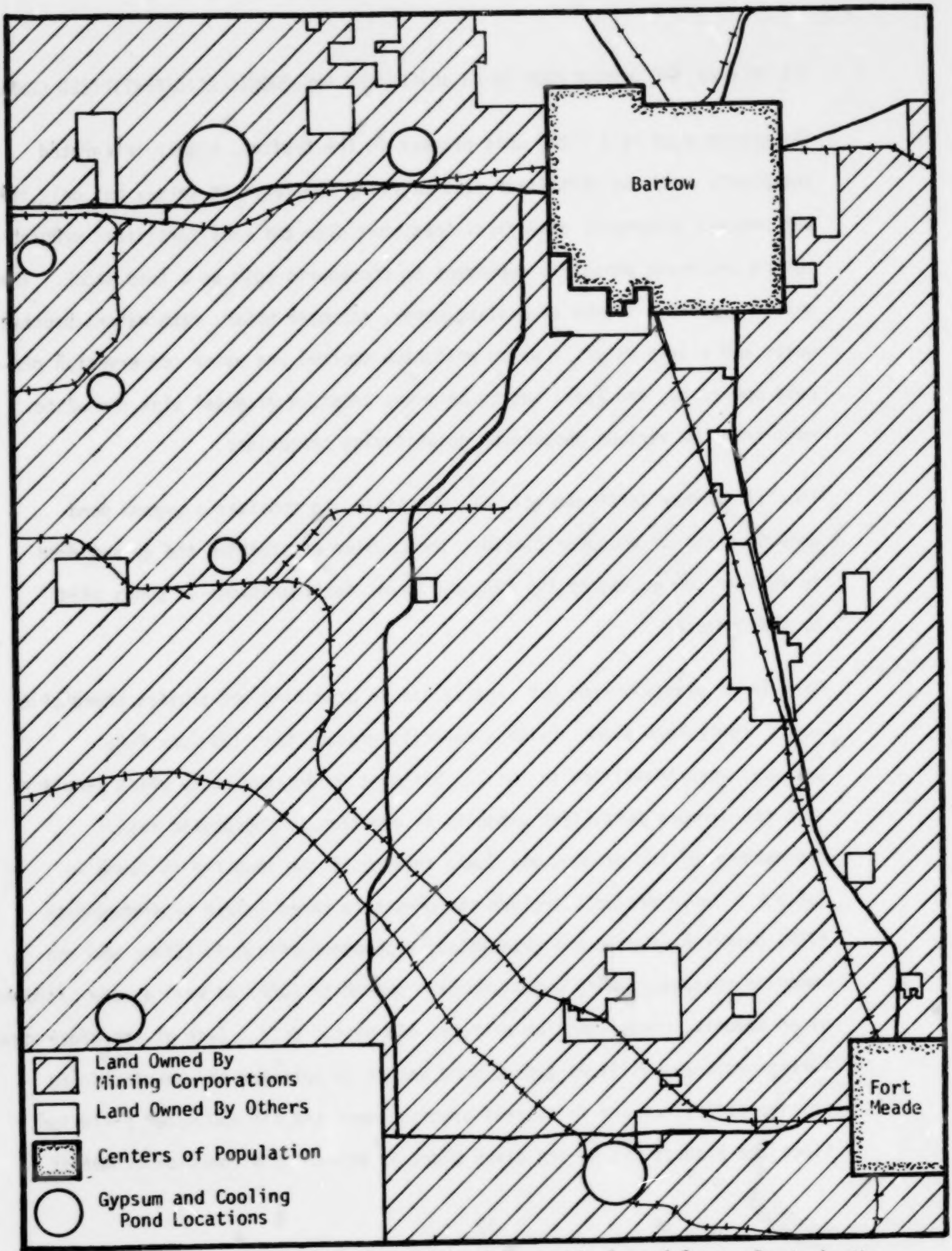

Bartow
Fort Meade
Land Owned By Mining Corporations
Land Owned By Others
Centers of Population
Gypsum and Cooling Pond Locations

Figure 1.5 Map Showing General Land Ownership Around Gypsum Ponds in the Bartow-Fort Meade Area of Central Florida.

2.0 THE ROLE OF THE GYPSUM POND IN AN INTEGRATED PHOSPHORIC ACID/FERTILIZER COMPLEX

The gypsum pond is a vital unit process in the typical, highly integrated phosphoric acid and fertilizer manufacturing complex. It serves not only the wet process phosphoric acid facilities, but also the many fertilizer manufacturing processes which are dependent on phosphoric acid as a feed stock. The gypsum pond is a source of cooling water, scrubber water, wash water, process water and slurry water; a water pollution control and water conservation process operation; and last, but by no means least, a disposal sink for waste rock from the various phosphorus solubilizing operations.

Thus it is very difficult, if not impossible, to consider a gypsum pond only in terms of phosphoric acid. The problem of studying the gypsum pond is further compounded by the many different configurations of ponds used by the industry.

Only three plants in the U.S. specialize in producing wet process phosphoric acid. Forty-four plants (with a capacity greater than 120 tons P_2O_5 per day) were identified in the EPA Effluent Guidelines Study which manufacture one or more fertilizer products in addition to phosphoric acid. A breakdown of the product mix found throughout the industry is found in Table 2.1. These products include the phosphate based Triple Superphosphate (TSP) both run-of-pile and granulated; Superphosphoric Acid (SPA); and monammonium phosphate (MAP) and diammonium phosphate (DAP) as well as the nitrogen based ammonia, urea, ammonium nitrate, and nitric acid. Each of the above manufacturing processes utilizes gypsum pond waters to optimize the manufacturing process efficiency and to control process generated air and water pollution. Since the product mix at any given plant is primarily a function of market

Reproduced from best available copy.

TABLE 2.1 Integration of Production In The Fertilizer Industry

Source: (EPA-440/1-74-011-a)

No. of Companies	NH_3	U	N.A.	A.N.	S.A.	Wet	A.P.	TSP	SPA	No. of Plants
22	X									22
2				X						2
2		X								2
4	X	X								12
3	X	X		X						9
3					1/	X				3
1								X		1
3					1/	X		X		6
6							X			6
1	X	X					X			3
7					1/	X	X			14
3					1/	X	X	X		9
1	X				1/	X	X	X		4
1					1/	X	X	X	X	4
3	X									6
1	X			X						3
2	X		X							4
13			X	X						26
5	X		X	X						15
3	X	X	X							9
1		X	X	X						3
16	X	X	X	X						64
1			X	X			X			3
2	X		X	X			X			8
1	X	X	X				X			4
4	X	X	X	X			X			20
1	X	X	X	X	1/	X	X		X	7
1	X		X	X						4
1	X	X	X	X						5
2	X				X					4
1					X					
2					X	X	X			6
2	X				X	X	X			8
1	X	X			X	X	X			5
1					X	X	X	X		4
1	X				X	X	X	X		5
1					X	X	X	X	X	15
7					X					14
1					X	X	X			4
1	X				X	X	X	X		6
1	X		X	X	X					4
1	X	X	X	X	X					5
:	X	X	X	X	X	X	X			7
160										390

1/ Not identified individually in data used to develop this list, but must assume existence of sulphuric acid facility as intermediate to wet acid production.

2/ Only 109 firms--includes more than one location of plant operations for some firms.

U	Urea
N.A.	Nitric acid
A.N.	Ammonium nitrate
S.A.	Sulfuric acid
Wet	Wet phosphoric acid
A.P.	Ammonium phosphate
TSP	Triple Superphosphate
SPA	Superphosphate acid

conditions, transportation costs, and geographical location, it is not feasible to attempt to characterize all of the possible combinations in this study. Instead the major manufacturing processes for each phosphate based product will be discussed and the unit operations or other sources of impact on a gypsum pond for each process will be identified. These unit operations will be characterized with respect to fluoride contribution to the gypsum pond. A flow and mass balance for an integrated phosphate complex will be developed.

2.1 PROCESS DESCRIPTIONS

2.1.1 Phosphoric Acid - Furnace Method

Phosphoric acid is produced by the furnace method. However, this process is primarily oriented towards the recovery of elemental phosphorus and high quality technical grade phosphoric acid rather than fertilizer and merchant grade acid. Furthermore, the furnace process does not require the use of gypsum ponds. Consequently the furnace method will not be discussed.

2.1.2 Phosphoric Acid - Wet Process

The most common method of producing phosphoric acid is by a wet process utilizing sulfuric acid. The use of this process is the reason for the existence of the gypsum pond. It is general practice throughout the industry to integrate one or more phosphate fertilizer manufacturing operations into the same complex with the wet process phosphoric plant. Phosphate rock is a complex material; the principal mineral constituent, fluorapatite, contains calcium, phosphate, fluoride, carbonate, and many other elements or groups bound together in a crystal lattice. Analysis of several typical grades of Florida rock is found in Table 2.2 When the rock is treated with a strong mineral acid, the apatite lattice is destroyed and the phosphate constituent is solubilized as phosphoric acid. The overall reaction with sulfuric acid is as follows:

1. The tricalcium phosphate constituent is converted to phosphoric acid and calcium sulfate.

$$Ca_3(PO_4)_2 + H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 \qquad (2.1)$$

2. The calcium fluoride constituent of the fluorapatite reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate.

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \qquad (2.2)$$

3. The calcium carbonate constituent is converted to carbon dioxide and calcium sulfate.

$$CaCO_3 + H_2SO_4 \rightarrow CO_2 + CaSO_4 + H_2O \qquad (2.3)$$

The entire reaction between the major constituents and sulfuric acid is as follows:

$$\begin{gathered} Ca_{10}(PO_4)_6F_2CaCO_3 + 11H_2SO_4 + nH_2O(liq) \rightarrow 6H_3PO_4(aq) + \\ 11CaSO_4nH_2O + 2HF(aq) + H_2O + CO_2 \qquad (2.4) \end{gathered}$$

where n may equal 0, 1/2 or 2 depending on the form of the hydrated $CaSO_4$, anhydrite, hemidydrate and dihydrate, respectively.

Table 2.2 Typical Composition and Particle Size of Commercial Grades of Florida Phosphate Rock[a]. (Legal, p. 21)

	SPECIFIED BPL RANGE				
	68/66	70/68	72/70	75/74	77/76
BPL (by analysis)	68.15	70.16	72.14	75.17	77.12
P_2O_5 equiv.	31.18	32.10	33.00	34.39	35.28
H_2O	1.3	1.0	1.0	1.0	1.0
Fe_2O_3	1.33	1.25	1.07	1.03	0.84
Al_2O_3	1.76	0.96	0.83	0.82	0.56
Organic	2.18	1.74	1.76	1.73	0.56
SiO_2	9.48	8.68	6.46	4.59	1.70
CO_2	3.48	3.05	2.87	2.65	2.02
F_2	3.60	3.67	3.62	3.78	2.98
CaO	45.05	46.12	48.10	50.14	51.53
SO_3	1.05	1.02	1.11	0.74	0.66

Screen analysis

	% larger or smaller than indicated mesh size				
Specified size[b]	+50	+70	+100	+200	-200
85% through 100 mesh	1.5	5.5	14.0	25.0	75.0
90% through 100 mesh	1.0	4.0	10.0	24.1	75.9

[a] Dry basis.
[b] All grades.

The excess fluoride present in the phosphate rock also reacts with phosphoric acid and sulfuric acid for form HF.

$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF \quad (2.5)$$

$$CaF_2 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HF \quad (2.6)$$

The HF then reacts with excess silica:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (2.7)$$

During the acid concentration steps, a considerable portion of the fluosilicic acid dissociates to form HF and SiF_4:

$$H_2SiF_6 \rightarrow SiF_4 + 2HF \quad (2.8)$$

The fumes resulting from H_2SiF_6 volatilization are scrubbed with water, however, regenerating the H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2 \quad (2.9)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (2.10)$$

which is pumped to the ponds with the gypsum slurry.

The most common method of producing wet process phosphoric acid is with the use of sulfuric acid in the dihydrate process. Typical analysis of this acid is found in Table 1.3. However, there are several other processes which are worthy of mention because of the significant effects their increased acceptance and use would have on the use of gypsum ponds. These processes include the hemihydrate process, the hemihydrate-dihydrate processes, the anhydrite processes, nitric acid processes and hydrochloric acid processes. Only the sulfuric acid processes will be discussed at this time, however, because they are most commonly used in the United States. The nitric and hydrochloric acid processes are used in Europe to produce directly complex fertilizers rather than phosphoric acid.

Table 2.3 Composition of Filtered Wet-Process Phosphoric Acids (Slack, p. 656)

Rock source	Acid composition, %										Composition of suspended solids
	P_2O_5	CaO	F	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	SO_3	
Florida[a]	27.3	0.15	1.7	0.6	1.1	0.28	0.03	0.08		1.2	B, A, C
b	28.4	0.1	1.5	1.1	2.0					3.9	
b	31.2	1.0	1.4	0.8	1.7					0.2	
b	26.3	0.4	2.0	0.5	1.1				1.1	1.0	
b	30.2	0.1	2.0	1.9	1.1				1.6	3.1	
c	30.0	1.26	2.36	1.08	0.86		0.06	0.01	1.21	3.72	
c,d	27.0-31.9	0.01-0.8	0.9-3.1	0.2-1.6	0.8-2.4				0.2-0.6	0.4-4.6	A, C
Western[a]	23.2	0.22	1.2	0.8	0.6	0.33	0.05	0.13		1.0	A, C
c	30.0	0.21	1.36	1.01	0.42	0.05	0.06	0.01	0.74	2.63	
Tennessee[c]	30.0	0.37	2.54	2.66	2.27		0.07	0.43	0.1	1.49	

[a] Composition of clear, supernatant acid after cessation of precipitation; compounds identified in solids: A=$CaSO_4\ 2H_2O$; B= $Ca_4SO_4(AlF_6)(SiF_6)OH\ 12H_2O$; C=$(Na, K)_2SiF_6$.

[b] Compositions of acids include any suspended solid material in shipped acids.

[c] Data taken from Table II of Hill (7) and recalculated to 30% P_2O_5 basis for comparison

[d] Composite analyses of 21 product acids.

The basic objective of any method of preparing phosphoric acid from phosphate rock and sulfuric acid is to obtain the highest concentration of phosphoric acid possible with the maximum yield. The yield is dependent on the completeness of the reaction of rock and sulfuric acid and on the efficiency of the separation of phosphoric acid from calcium sulfate. The quantity of wash water required to remove essentially all the P_2O_5 from the calcium sulfate during filtration determines the concentration. Consequently, the characteristics of the calcium sulfate crystals formed during the reaction are the most important fundamental factors in phosphoric acid production. The temperature of the reaction mass and the phosphoric acid concentration are the controlling factors governing the degree of hydration of the calcium sulfate. The influence of temperature and concentration on the state of hydration and the stability of the calcium sulfate has been studied by many investigators and phase diagrams have been developed. All the commercial wet processes for phosphoric acid are based on conditions, as defined in these phase diagrams (Figure 2.1), that give stable, filterable forms of calcium sulfate.

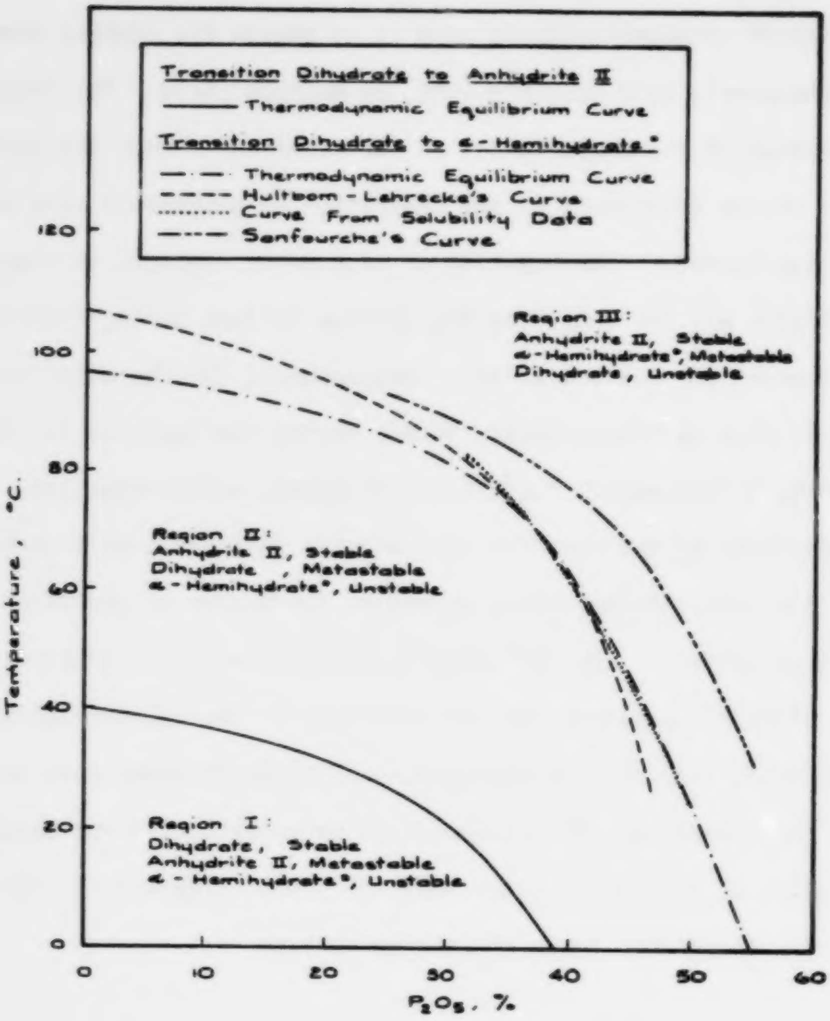


Figure 2.1 Phase Equilibrium Diagram for $CaSO_4$-P_2O_5-H_2O System (Dahlgren, p. 94)

2.1.3 Dihydrate Process

The dihydrate process produces 28-32% P_2O_5 phosphoric acid by acidulating ground phosphate rock at a temperature of 160 to 185°F. These conditions result in the formation of calcium sulfate in the dihydrate form.

The typical dihydrate process (Figure 2.2) used prior to the early 1960's, and still in widespread use today, involves the reaction of sulfuric acid and phosphate rock in a series or "train" of agitated reactor tanks through which the slurry cascades by gravity. These trains may consist of four or more tanks, and retention time in the system ranges from 4 to 8 hours. The initial step consists of premixing sulfuric acid with recycled weak phosphoric acid and recirculated phosphoric acid slurry. Dry, ground rock is added to this mixture, in slightly less than the stoichiometric proportion to maintain a slight excess of sulfuric acid in the system. The slurry then flows through the successive reactor tanks in which temperature and acid concentration are controlled to ensure completeness of reaction and good growth of gypsum crystals to the size necessary for effecting good separation of acid and gypsum in the filtration step. After leaving the last stage reactor tank, the slurry is split into two streams in a ratio of about 15 to 1. The larger stream is recirculated to the premixing tank to be intermixed with the fresh sulfuric acid; the smaller is pumped to a filter for separation and washing of the gypsum crystals. Filter operation usually involves three continuous stages. The product acid, containing 28-32% P_2O_5, is separated from

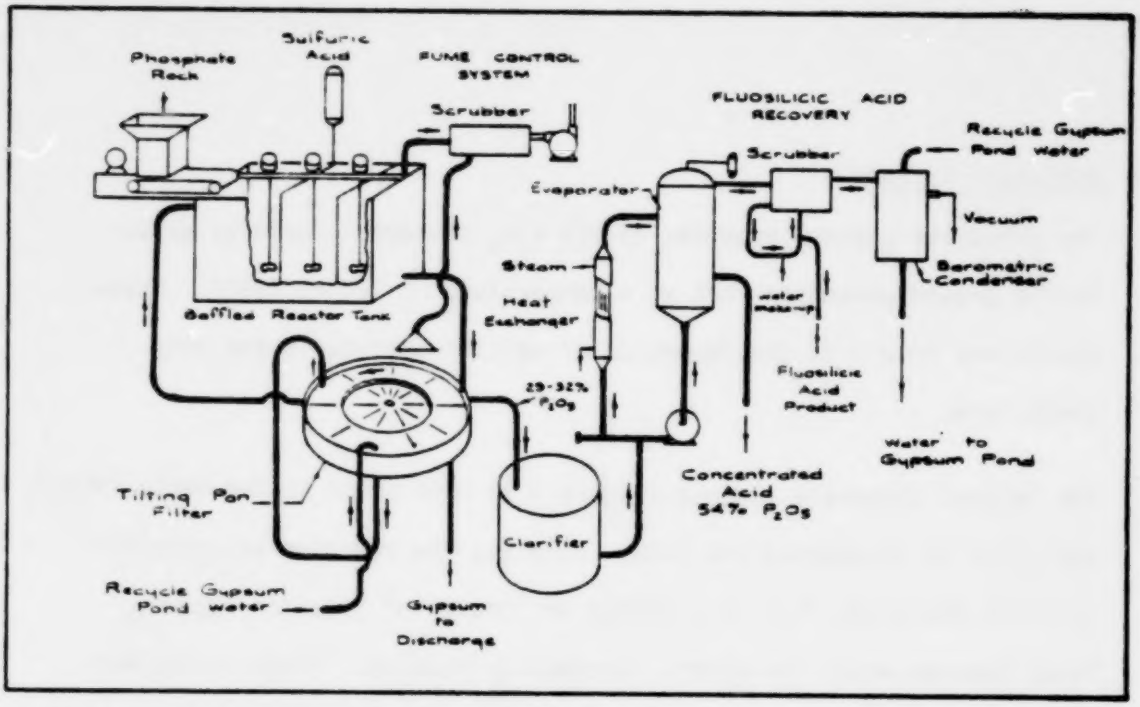


Figure 2.2 Typical Dihydrate Process With Vacuum Acid Concentration and Fluosilicic Acid Recovery (Slack, p. 31)

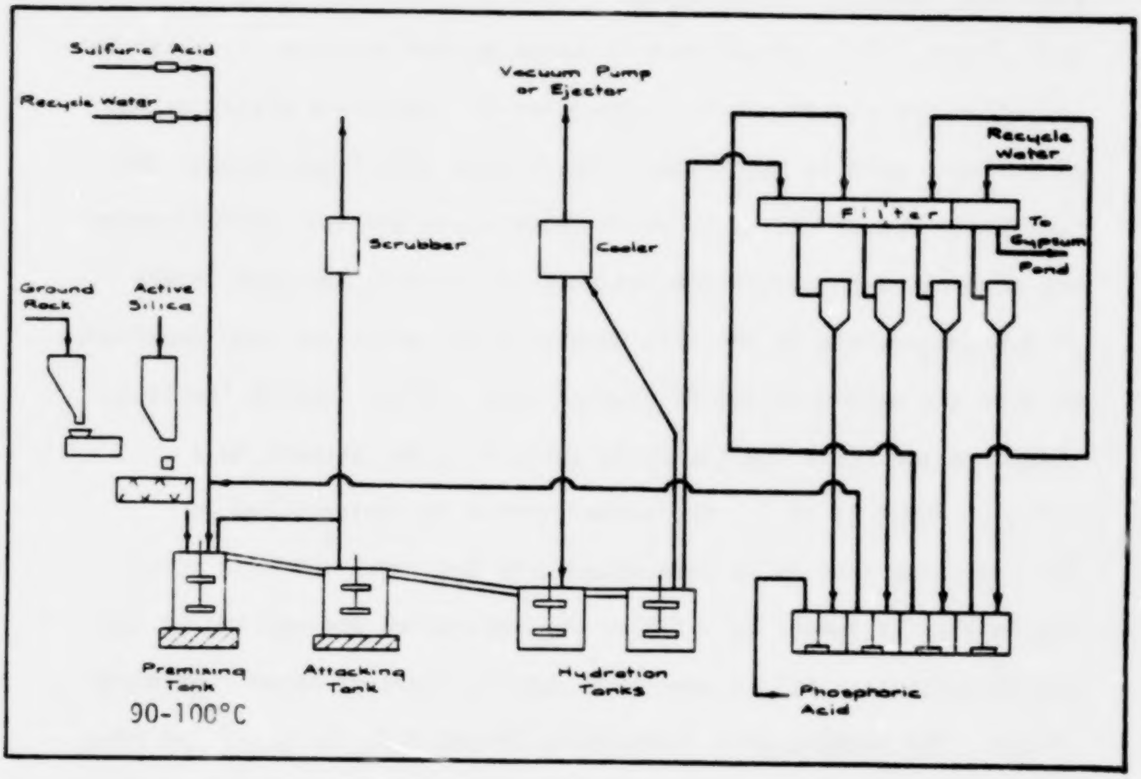


Figure 2.3 Hemihydrate - Dihydrate Phosphoric Acid Process (Takeuchi, p. 303)

the gypsum in the first stage, and the phosphoric acid remaining is washed from the gypsum residue during the second and third stages. Recycled gyp pond water is frequently used as the wash on the third stage; the filtrate from this stage is circulated over the gypsum in the second stage, where the acid concentration reaches about 20% P_2O_5, and is then pumped back to the premixing tank. The washed gypsum cake discharged from the third stage is usually reslurried with water and pumped to a disposal area. The product acid from the filter is concentrated to the desired strength in vacuum evaporators or submerged combustion concentrators.

Although the new plants constructed since 1960 employ the same basic principles as those used in the old process, improved engineering design and materials of construction have decreased capital and operating costs per unit of capacity and have improved overall operating efficiency. In these plants (Figure 2.2) single-tank, multiple-compartment reactors replace the multiple-tank train. Precise design of the tank interior is important to assure complete reaction of the rock and sulfuric acid and prevent the bypassing of unreacted rock. A series of agitators and baffles forces circulation of the slurry through prearranged paths to give the same effect as the slurry recirculation and cascade arrangement in the train system.

In a typical Florida operation 68 BPL (31.1% P_2O_5) rock (ground to 50-55% minus 200 mesh in a ball mill) is measured through gravimetric feeders to the slurry in the first compartment of the reactor, where it is mixed with sulfuric acid (93%) and recirculated slurry. Good control of raw material feeding and of slurry composition is essential to assure proper operating conditions throughout the entire 5-6 hour residence time required for reaction and gypsum crystallization. The rock:acid ratio, which must be held within narrow limits, is controlled by the electronic proportioning of the acid flow with the phosphate rock feed. The weight of solids in the slurry (termed pulp solids content, or sometimes slurry density), is controlled by varying the amount of recycled acid. Upsets may occur which require wasting of the slurry to the gypsum pond to regain the proper rock:acid ratio.

2.1.4 Hemihydrate Process

The hemihydrate process produces phosphoric acid at 38-42% P_2O_5 concentration by acidulating the phosphate rock at temperatures of 90-135°C. The higher concentration of the product acid reduces the number of evaporator stages required for concentration to 54% merchant grade acid. This process has been successfully demonstrated in Europe (AB Forenade), Japan (Taki) and the U.S. (TVA), however, it has not been accepted by the industry due to difficulties in controlling the operation.

2.1.5 Hemihydrate-dihydrate Process

The hemihydrate-dihydrate process involves the precipitation of calcium sulfate in the hemihydrate form followed by recrystallization to dihydrate. This basic process has been extensively developed in Japan and Europe but has been evaluated only on the pilot plant scale in the U.S. This process is claimed to have a high level of stability and reliability in plant operations, 97-98.5% recovery of P_2O_5 from the phosphate rock (allegedly higher than by the dihydrate process), and recovery of by-product gypsum (1.2 to 1.5 tons gypsum/ton phosphate rock) that is of high enough quality to use in making gypsum plaster, gypsum wallboard, portland cement and for chemicals such as in the gypsum-ammonium sulfate process.

The spent gypsum from the hemihydrate-dihydrate process is slurried to a storage pond area where the by-product gypsum is recovered by either filtration or settling.

A flow sheet of a hemihydrate-dihydrate process is shown in Figure 2.3. Operating features of the various process steps are as follows:

Decomposition - Raw phosphate rock is ground to 60 to 80% through 200 mesh and transported to the rock hopper at the phosphoric acid plant. After passage through a constant feed weigher, the rock is moved by a screw conveyor to the premixing tank; active silica is also weighed and is fed by the same screw. Sulfuric acid is measured by a flow meter, diluted to the desired concentration (about 65%), and sent to the premixing tank where it is mixed with recycled phosphoric acid of about 20% P_2O_5 content. Silica is added at this point in the process to tie up HF as in SiF_4. It is possible to recover the SiF_4 as a H_2SiF_6 by-product. The temperature inside the premixing tank is maintained between 194 and 212°F by the sensible heat of the mixed acid and the reaction heat. Since mixing is rapid in the premixer, there is no opportunity for local points of high temperature to persist long enough for anhydrite formation. Severe foaming takes place during decomposition of the phosphate rock, requiring the use of a defoaming agent or other means for controlling foam. No such agent is required when calcined rock is used.

The slurry is thoroughly mixed in the premixing tank and then overflows into the attacking tank where decomposition proceeds. The retention time required for decomposition varies with the grade of phosphate rock but ordinarily about 2 hours is adequate.

In the course of decomposition, calcium sulfate produced by the decomposition should be completely converted to hemihydrate. Should gypsum form in this step, gypsum crystals produced in the subsequent hydration step will not be uniform and the tota P_2O_5 content of the gypsum will increase, reducing P_2O_5 yield and adversely affectin the quality of the by-product gypsum. It is necessary, therefore, to carefully control the concentration of phosphoric acid, the amount of excess sulfuric acid, and the decomposition temperature. Off-gas from the premixing and attacking tanks is collected in the duct and washed in the Venturi scrubber to remove fluorine compounds. All the tanks are cylindrical and equipped with agitators. Since corrosion is a more severe problem at the relatively high attack temperature used, the tanks are lined with carbon bricks and with a rubber resistant to high temperature. The agitators are also lined with such rubber.

Hydration (Recrystalization) - Slurry from the decomposition step overflows into the hydration tank where it is mixed with cooled, recycled dihydrate slurry, giving a temperature between 50 and 58°C. The slurry recycles from the last hydration tank through the cooling tower to the first hydration tank. The recycling also performs the function of maintaining uniform Ca^{2+} concentration and concentrating the slurry. Owing to the rapid increase in supersaturation, fine gypsum crystals form in the recycling slurry and act as crystal seeds, making it unnecessary to introduce seeds from outside the system.

The volume of recycled slurry is determined by the operating conditions, but it is several times the volume of slurry fed to the filter. In the hydration tanks hemihydrate recrystallizes gradually to dihydrate, and at the outlet of the second tank the crystals are large enough for easy filtration and washing. The degree of phosphate rock decomposition is 99 to 99.5%.

The hydration tank and the cooling tower are rubber-lined, and the slurry pump is made of a special corrosion-resistant stainless steel.

Filtration - Any type of conventional filter can be used, such as tilting-pan or traveling-pan filters. The gypsum cake formed on the pans has a thickness of 1.5-2.0 in. After counter-current washing it is removed from the pans in the form of a cake containing 20 to 25% water. The product phosphoric acid (about 30% P_2O_5) is sent to the storage tank. Dilute acid (about 20% P_2O_5) from the second stage of filtration is recycled and mixed with the feed sulfuric acid. The gypsum cake from the filter is repulped with water and sent to the gypsum storage yard, where it is separated from the water by means of settling or filtration. It is sold to wallboard, plaster, and cement manufacturers.

2.1.6 Phosphate Rock Grinding and Drying

Phosphate rock that has been mined and beneficiated is generally too coarse to be used directly in acidulation to phosphoric acid. The rock is, therefore, processed through equipment to mechanically reduce it to the particle size required for optimum phosphoric acid plant process efficiency.

Size reduction is accomplished with ball, roll or bowl mills. Phosphate rock is fed into the mills and mechanically ground. After the rock enters the mill system, all flow through the sizing and reclamation circuits is by pneumatic means. Air is constantly exhausted from the mill system to prevent precipitation of moisture generated from the rock as a result of grinding. Normally, the exhaust air passes through a bag type air cleaner to remove entrained rock particulates before discharge to the atmosphere.

Phosphate rock size reduction in all existing fertilizer plants is an entirely dry processing circuit and does not directly involve liquid streams. Minor quantities of water are used for indirect cooling of lubricating oil and mechanical equipment such as bearings.

Rock grinding operations in the future will also utilize a wet grinding circuit rather than the current dry grinding practice (Long, Slack). This change is prompted by a combination of lower capital costs and the elimination of the gas effluent streams associated with both the rock drying and grinding operations. Use of this new technique will not change the self-contained nature of the rock grinding circuit. There will be no liquid effluents other than those mentioned in the dry grinding process.

2.1.7 Acid Concentration and Defluorinated Superphosphoric Acid

Wet-process phosphoric acid (30% P_2O_5) from the dihydrate process is not directly suited for use in end products and must be concentrated by evaporation. A concentration of 40 to 42% P_2O_5 is required in producing ammonium phosphate (AP) and granulated triple superphosphate (GTSP) made by the slurry process, and 52 to 53% P_2O_5 acid is needed in making run-of-pile (ROP) triple superphosphate and shipping-grade (merchant) acid. Wet acid produced by a hemihydrate process at 40 to 42% P_2O_5 or by an anhydrite process at 52 to 54% P_2O_5 is directly suited for use in the manufacture of such fertilizer products.

The term defluorinated phosphoric acid is a bit misleading to persons associated with the fertilizer industry. The reason is that acid defluorination is inherently included in the process of evaporating commercial wet process 54% P_2O_5 phosphoric acid to the superphosphoric acid (68-72% P_2O_5) concentration level. To fertilizer people therefore, the principal U.S. defluorinated acid process is better known as a superphosphoric acid unit.

Defluorinated phosphoric acid is used primarily as a raw material for production of mixed fertilizer goods - both dry and liquid types. It is also mixed with limestone in the manufacture of dicalcium phosphate for use as an animal feed supplement. Approximately 67% of the estimated U.S. 835,000 annual tons P_2O_5 quantity of defluorinated acid is used in fertilizer manufacture and 33% in the production of dicalcium phosphate. The degree of defluorination required to meet animal feed regulations is that the P to F ratio be at least 100 to 1. (EPA 440/1-75/043)

The concentration and defluorination of phosphoric acid is a difficult operation, as the acid is corrosive. Scaling of equipment is also a problem. Equipment designs historically have been of five types: (1) forced-circulation vacuum (Figure 2.4), (2) thermal-siphon vacuum, (3) falling-film vacuum, (4) submerged combustion (Figure 2.5) and (5) hot gas evaporation. All five methods have been used commercially, but the forced-circulation vacuum process with steam as the heat source is the most popular in modern phosphoric acid plants.

Another method of defluorinating wet process phosphoric acid has come into commercial use in the past few years (Figure 2.6). This process also uses merchant grade wet process 54% phosphoric acid as the raw material. In this process, silica is mixed with the phosphoric acid to aid in the release and volatilization of fluorine from the liquid. The mechanism for fluoride

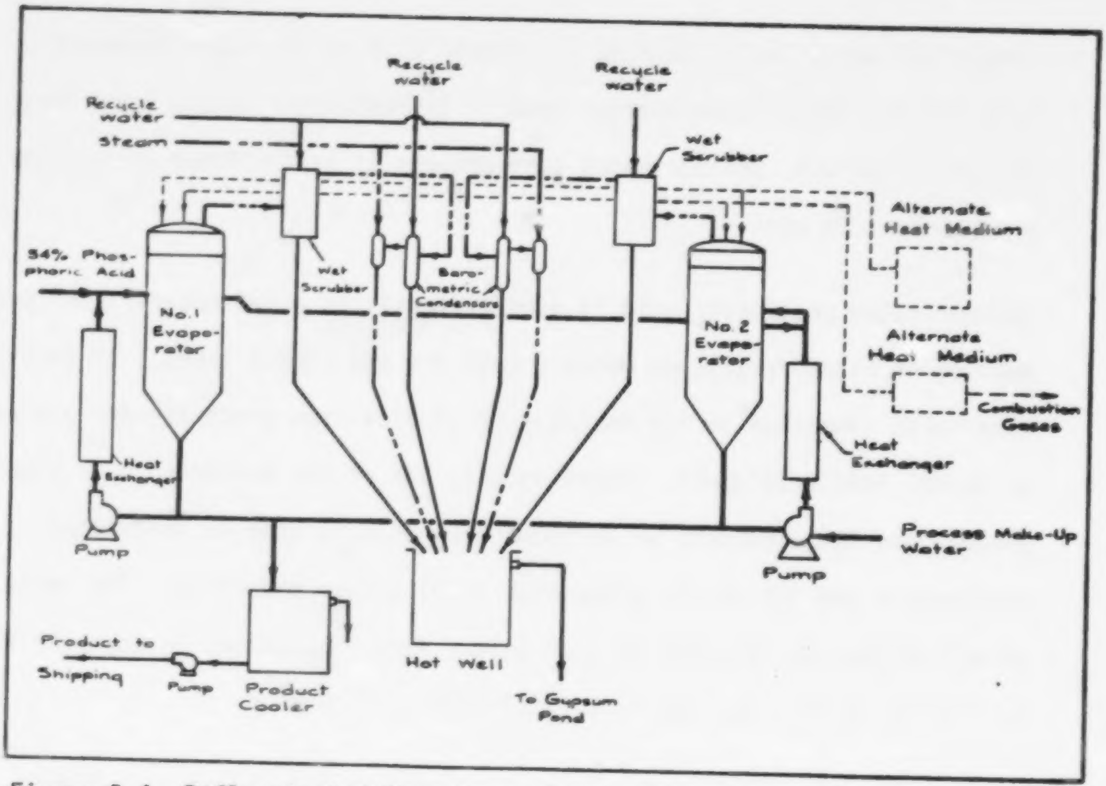


Figure 2.4 Defluorinated Phosphoric Acid - Vacuum Process (EPA 440/1-53/043)

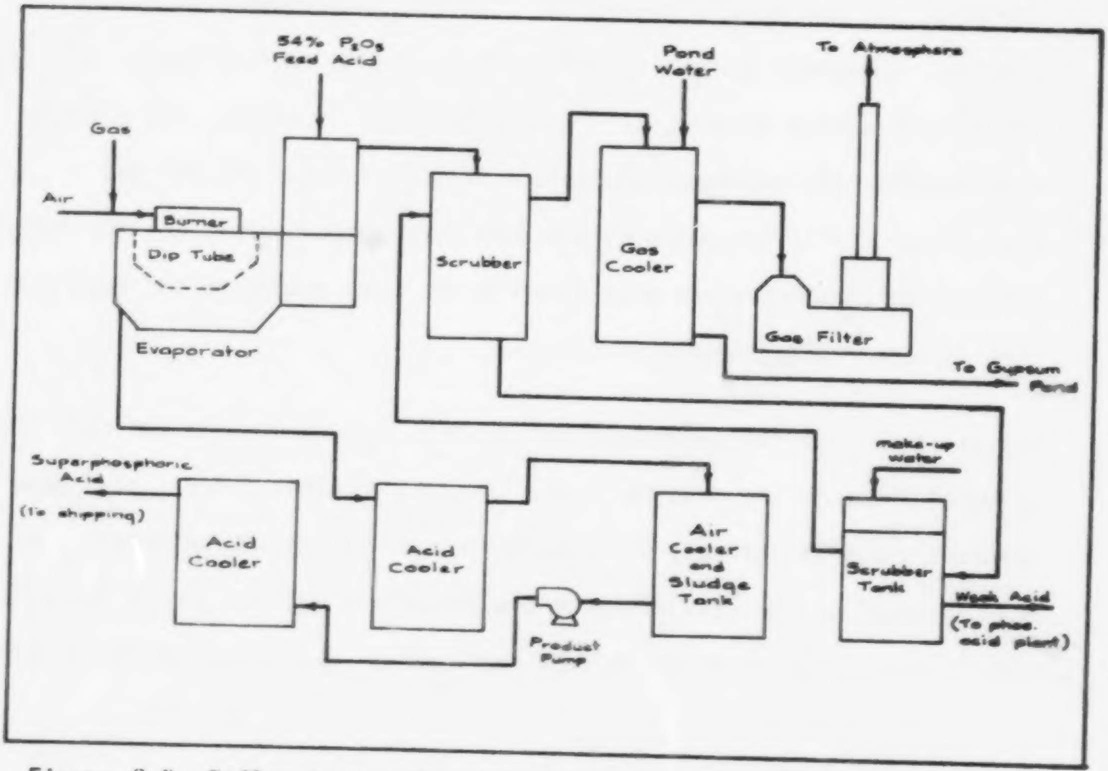


Figure 2.5 Defluorinated Phosphoric Acid - Submerged Combustion (EPA 440/1-75/043)

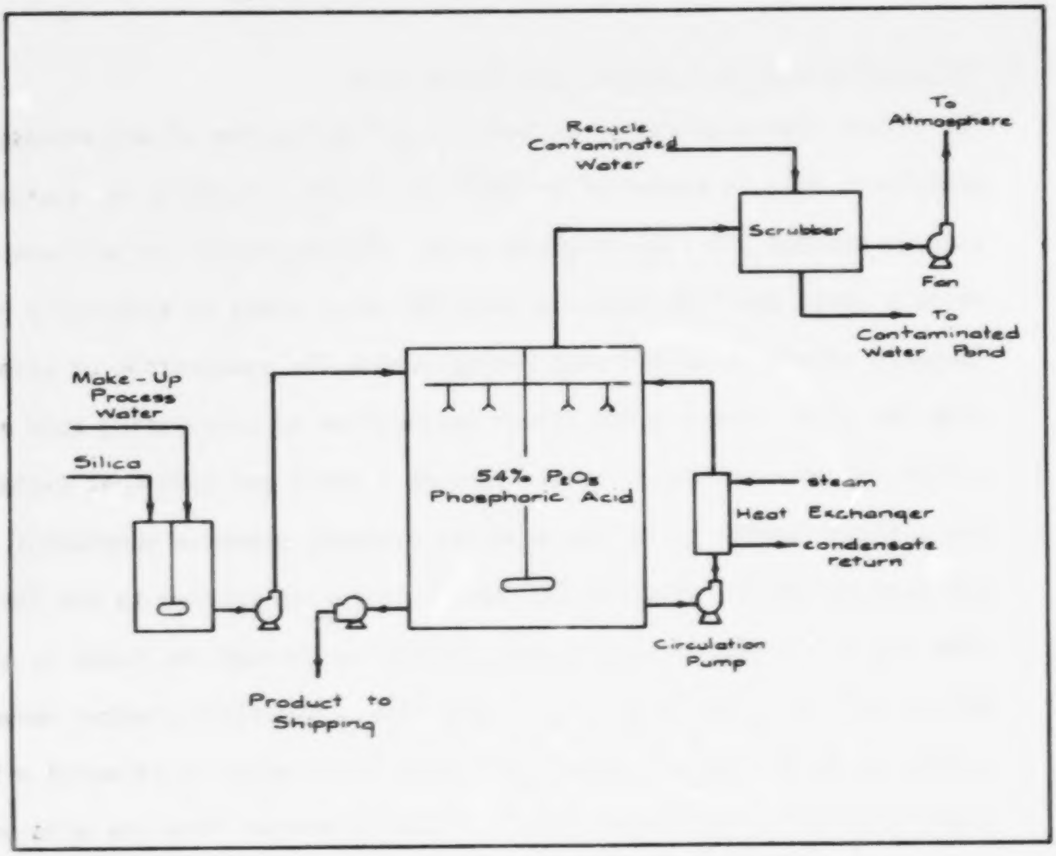


Figure 2.6 Defluorinated Phosphoric Acid - Aeration Process (EPA 440/1-75/043)

removal from the acid is aeration (EPA 440/1-75/043).

2.1.8 Defluorinated Acid - Vacuum Type Evaporation

The vacuum type evaporation method for defluorination of wet process phosphoric acid is essentially identical to the procedure and equipment used to produce 54% P_2O_5 strength acid. Defluorination is performed in vessels which use high pressure (450-550 psig) steam or externally heated Dowtherm solutions as the heat energy source for evaporation of water from the acid. These units affect evaporation by circulating acid at a high volume rate consecutively through a shell and tube heat exchanger and a flash chamber under low absolute (vacuum) pressure conditions. In the heat exchanger, steam or Dowtherm solution is applied to the shell side and acid flows through tubes. Acid flow through the tubes is of the wetted wall type rather than full tube flow. The flash chamber serves to provide a large liquid surface area where water vapor is released without significant acid entrainment loss. Fluoride removal from the acid occurs concurrently with the water vapor release. Both of these gases pass to a barometric condenser and are absorbed in the condenser water. Dependent upon the quality of superphosphoric acid being produced (e.g. 30% or 50-60% conversion to polyphosphates), either a single unit or a series of two units may be used to accomplish the evaporation and/or defluorination required. Fluosilicic acid may be easily recovered from this type evaporation (Figure 2.2 and 2.4).

2.1.9 Defluorinated Acid - Submerged Combustion

A second method of phosphoric acid defluorination (Figure 2.5) is by the direct contact of hot combustion gases with the acid. In this method a combustion chamber fitted with one or more fuel oil or gas burners is mounted directly on top of an acid containment chamber. Pressurized hot gases from the fuel combustion are bubbled through the acid to an immersion depth of up to approximately 46 cm (18 inches). Acid in the containment chamber is maintained at a constant level by control of the low concentration feed acid flow. Evaporated and defluorinated product acid from the unit is continuous and is controlled by acid boiling point and/or temperature.

Gases (evaporated water, stripped hydrogen fluoride and silcon tetrafluoride) from the evaporation chamber flow to a series of gas cleaning and absorption equipment. First, entrained phosphoric acid is recovered from the gas stream and re-introduced to the unit or to the phosphoric acid plant. Following acid removal, the gases pass to a multi-stage direct contact condenser system where a high percentage of the contaminants are removed before exhaust to the atmosphere. Water can be used in all or only the final stages of the condenser system as a condensing and scrubbing medium.

2.1.10 Defluorinated Acid - Aeration

This method of defluorinating phosphoric acid is the most recent proprietary method to come into commercial use (Figure 2.6). Relatively small quantities of diatomaceous silica or spray dried silica gel with high surface area characteristics are mixed with commercial 54% P_2O_5 phosphoric acid. This silica material also serves to supply sufficient silica for conversion of the minor quantity of hydrogen fluoride (HF) present in the impure phosphoric acid to fluosilicic acid (H_2SiF_6). Fluosilicic acid at an adequate temperature in turn breaks down to SiF_4 and HF and by simple aeration is stripped from the heated mixture. The gaseous effluent stream is maintained above its dew point until it enters the gas scrubber.

At this point the gas stream is contacted with water to remove contaminants before release to the atmosphere. Phosphoric acid (54% P_2O_5) can be defluorinated by this method to a weight ratio of P to F of 100 to 1 or better.

A major part of the impurities in filter acid is removed during concentration. In Table 2.4 several analyses of acids obtained from operating plants are given; they illustrate major reduction in impurity content between filter acid and concentrated acid, particularly with respect to fluorine and silica. The impurity-to-P_2O_5 ratio decreased significantly for all impurities.

All concentrated acids contain solid material resulting from post-precipitation of impurities. The compositions of concentrated acids and the solids separated from them are given in Table 2.5. As the solids in these acids were separated without washing, adhering phosphoric acid is included in the analysis. For some of the acids, which presumably had little or no clarification, the precipitates contained large amounts of CaO, SO_4, F, and SiO_2, indicating the presence of calcium sulfate and fluosilicates. Others, however, had relatively low solids content, and Fe_2O_3 was an important constituent of the solids. The major precipitating phase, forming in acids after concentration and clarification, has been identified as a complex potassium-iron-alumina-phosphate compound. Separated solids are either discharged to the gypsum pond or used as a solids conditioner in the manufacture of granular superphosphate.

Table 2.4 Effect of Concentration on Composition of Wet-Process Phosphoric Acids (Legal, p. 47)

Kind of rock	% by weight							
	P_2O_5	SO_3	CaO	Fe_2O_3	Al_2O_3	F	SiO_2	MgO
Concentrated acids								
Florida	54.6	3.6	0.3	1.3	0.6	--	--	--
Unknown	53.8	2.8	0.1	1.4	1.3	0.7	0.4	0.4
Florida	52.8	2.7	0.1	1.1	0.8	0.4	0.2	0.5
Florida	54.8	3.4	0.5	1.4	1.4	0.9	0.2	0.5
Western	51.1	1.9	0.1	1.1	2.8	1.4	--	--
Western	53.2	1.5	0.1	1.0	1.5	0.6	--	0.8
Western	54.2	1.0	1.3	0.7	1.5	1.1	0.6	0.5
Florida	58.2	2.3	0.0	1.3	1.7	0.6	0.2	0.7
Florida	50.6	3.0	0.1	1.4	1.5	0.8	--	--
Florida	53.4	1.5	0.1	1.7	1.1	0.9	0.1	0.5
Filter acids								
Florida	28.4	3.9	0.1	2.0	1.1	1.5	--	--
Florida	31.2	0.2	1.0	1.7	0.8	1.4	--	--
Florida	26.3	1.0	0.4	1.1	0.5	2.0	1.1	--
Florida	30.2	3.1	0.1	1.1	1.9	2.0	1.6	--
Unknown	30.0	1.8	0.3	1.4	3.0	2.4	--	--

Table 2.5 Analyses of Wet-Process Acids and of Solids Obtained by Filtering the Acids (Hein, p. 695)

Acid no.	Sample	Wt. %									
		P_2O_5	SO_3	CaO	Fe_2O_3	Al_2O_3	F	SiO_2	MgO	C	Solids
1	Total acid	53.8	2.6	0.1	1.4	0.8	0.5	0.2	0.3	0.1	1.9
	Solids	53.4	4.4	2.0	8.6	2.3	3.4	0.6	1.2	0.2	--
2	Total acid	52.8	2.6	0.1	1.1	0.8	0.4	0.2	0.5	0.6	3.1
	Solids	51.2	5.2	2.5	4.1	0.9	2.1	0.6	0.3	4.4	--
3	Total acid	54.2	1.0	1.3	0.7	1.5	1.1	0.6	0.5	0.0	13.4
	Solids	48.7	8.1	6.6	3.4	2.3	5.0	3.1	0.5	0.0	--
4	Total acid	51.5	2.1	1.0	2.1	1.1	1.8	0.6	0.7	0.3	20.3
	Solids	40.3	7.2	5.0	3.6	3.0	8.1	6.4	2.2	1.6	--

2.1.11 Normal Superphosphate

Normal superphosphate was, for many years, by far the most popular phosphate fertilizer. Since the mid-fifties, however, its popularity has been in a sharp decline and only in the past few years has the rate of decline started to moderate. The market share of this fertilizer has fallen from 68% in 1957 to 42% in 1965 and now appears to be leveling off at approximately 18%. The major reasons for this decline include such items as low P_2O_5 content (20%) with the associated increased cost of transportation per ton of nutrient and the trend to larger size plants.

Normal superphosphate can be manufactured in small inexpensive plants with low production costs per ton of P_2O_5 since the $CaSO_4$ formed in the acidulation of the rock is not separated from the final product. The process is simple and easy to operate, requiring less sulfur per ton of P_2O_5 than the production of phosphoric acid. The combination of low investment and simplicity, together with recognition of the beneficial fertilization effects of sulfur in the soil, assures that normal superphosphate production will not die out but sales will be limited to an area in close proximity to the plant site.

The two raw materials used in the production of normal superphosphate are 65-75% sulfuric acid and ground phosphate rock. Reaction between these two materials is both highly exothermic and rapid (Figure 2.7). The basic chemical reaction is shown by the following equation:

$$\underset{\text{Phosphate Rock}}{Ca_3(PO_4)_2} + \underset{\text{Sulfuric Acid}}{2H_2SO_4} + \underset{\text{Water}}{3H_2O} \rightarrow \underset{\text{Gypsum}}{2CaSO_4 \cdot 2H_2O} + \underset{\text{Normal Superphosphate}}{Ca(H_2PO_4)_2 \cdot H_2O} \qquad (2.11)$$

Ground phosphate rock (90% minus 100) is fed by a weigh feeder into a double-conical mixer (TVA), where it is thoroughly mixed with metered quantities of sulfuric acid. The sulfuric acid is diluted with water in the cone. The heat of dilution serves to heat the sulfuric acid to proper reaction temperature, and excess heat is dissipated by evaporation of extra water added. The rate of water addition and acid concentration may be varied to control the product moisture. The acid and water are fed into the cone mixer tangentially to provide the necessary mixing with the phosphate rock. The fresh superphosphate discharges from the cone mixer to a pug mill, where additional mixing takes place and reaction starts. From the pug mill the superphosphate drops onto the den conveyor, which has very low travel speed to allow about one hour for solidifying before reaching the cutter. The cutter slices the solid mass of crude product so that it may be conveyed to pile storage for "curing," or completion of the chemical reaction, which takes 10 to 20 days to reach an acceptable P_2O_5 availability as plant food. The continuous den is enclosed so that HF and SiF_4 fumes do not escape into the working area. These fumes are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere.

The wet scrubbers are the only significant source of wastewater from the process. When normal superphosphate is produced at an integrated fertilizer complex the scrubber will most likely utilize the gypsum pond water.

2.1.12 Triple Superphosphate

Triple superphosphate (TSP), with its 46.0% - 48.5% P_2O_5 content, is a high analysis phosphate fertilizer. As such, it provides transportation economy which has been instrumental in enlarging its share of the phosphate fertilizer market.

This product has in the 1950-1965 period taken over much of the market lost by normal superphosphate and currently accounts for approximately 24% of the total phosphate fertilizer market. TSP's share of the market for the near future is expected to remain relatively constant primarily Due to the tremendous growth of the ammonium phosphates. TSP production, unlike normal superphosphate, can be most economically produced close to the phosphate rock source. In the U.S. this means that approximately 83% of the total production if manufactured in Florida.

There are two principal types of TSP, Run-of-Pile (ROP) and Granular Triple Superphosphate (GTSP). Physical characteristics and processing conditions of the two materials are radically different. ROP material is essentially a non-uniform pulverized material which creates difficult air pollution problems in manufacture as well as difficult materials handling problems in shipment. GTSP is a hard, uniform, pelletized granule produced in process equipment which permits ready collection and treatment of dust and fumes. Most new plants will be the GTSP type.

Both processes utilize the same raw materials, ground phosphate rock and phosphoric acid. The basic chemical reaction is shown by the following equation:

$$Ca_3\,(PO_4)_2 + 4H_3PO_4 + 3H_2O \longrightarrow 3Ca(H_2PO_4)_2 \cdot H_2O \qquad (2.12)$$

Phosphate Rock ← Phosphoric Acid ← Water
Triple Superphosphate (Monocalcium Phosphate)

The wet scrubbers are the only significant sources of wastewater from the process. When triple superphosphate is produced at an integrated fertilizer complex the scrubber will most likely utilize the gypsum pond water.

2.1.13 Run-of-Pile - TSP

The ROP process train is essentially identical to the normal superphosphate process with the exception that phosphoric rather than sulfuric acid is used as the acidulating acid (Figure 2.7). Mixing of the 46-54% P_2O_5 phosphoric acid and phosphate rock normally is done in a cone mixer. The cone depends solely on the inertial energy of the acid for mixing power. On discharge from the mixer the slurry quickly (15-30 sec) becomes plastic and begins to solidify. Solidification with the evolution of the gas (as HF and SiF_4) takes place on a slow moving conveyor (den) enroute to the curing area. The solidified material, because of the gas evolution throughout the mass, takes on a honeycomb appearance. At the point of discharge from the den the material passes through a rotary mechanical cutter which breaks up the honeycombed ROP before it discharges onto the storage (curing) pile. Curing occurs in the storage pile and takes 2-4 weeks before the ROP is ready to be reclaimed from storage, sized and shipped.

2.1.14 Granular TSP

GTSP is produced quite differently (Figure 2.8). The phosphoric acid in this process may be appreciably lower in concentration (40% P_2O_5) than the 46-54% P_2O_5 acid used in ROP manufacture. Forty percent P_2O_5 acid and ground phosphate rock are mixed together in an agitated tank. The lower strength acid maintains the resultant slurry in a fluid state and allows

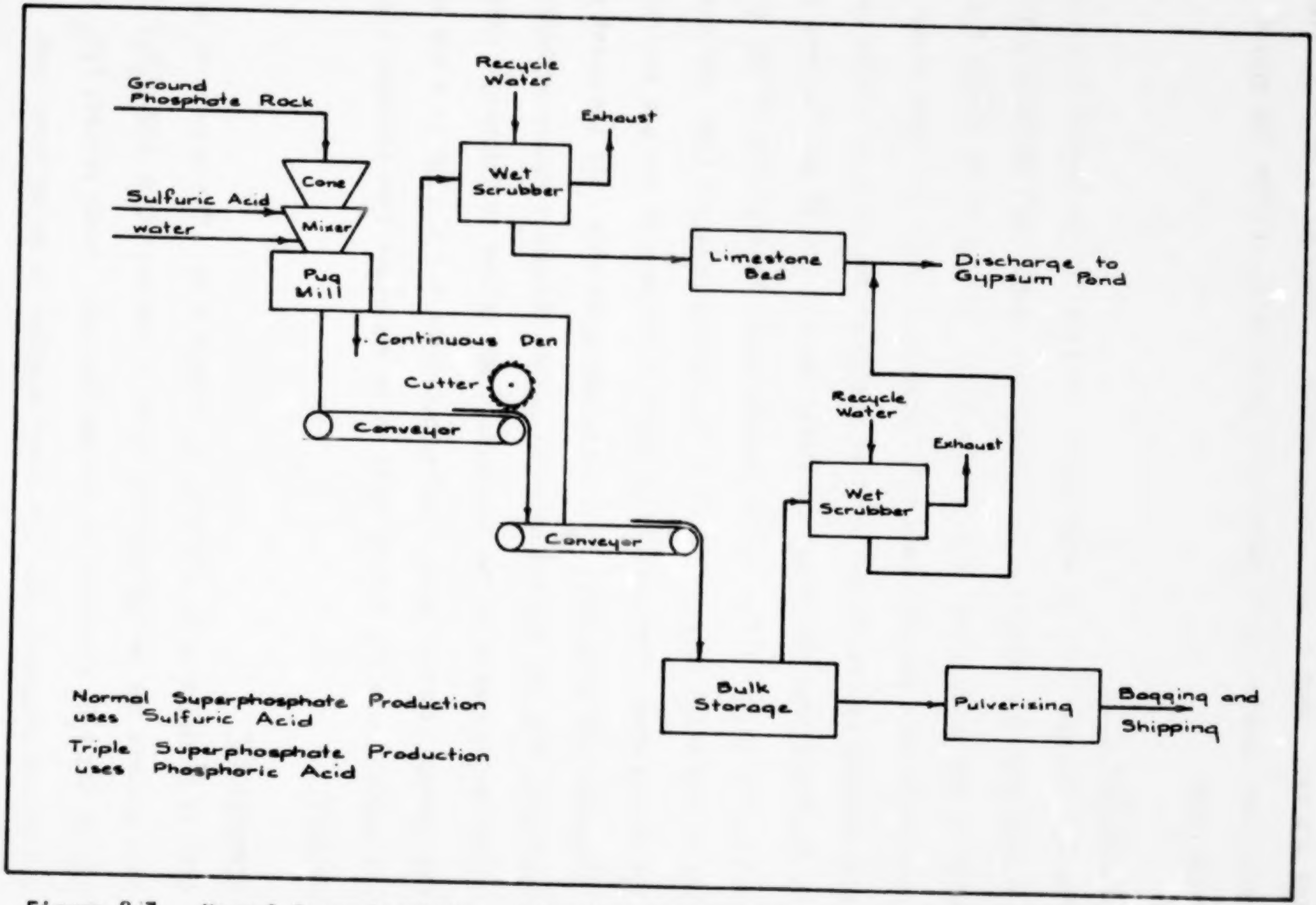


Figure 2.7 Normal Superphosphate and Triple Superphosphate - Run-of-Pile Process Schematic (Shrieve, p. 271)

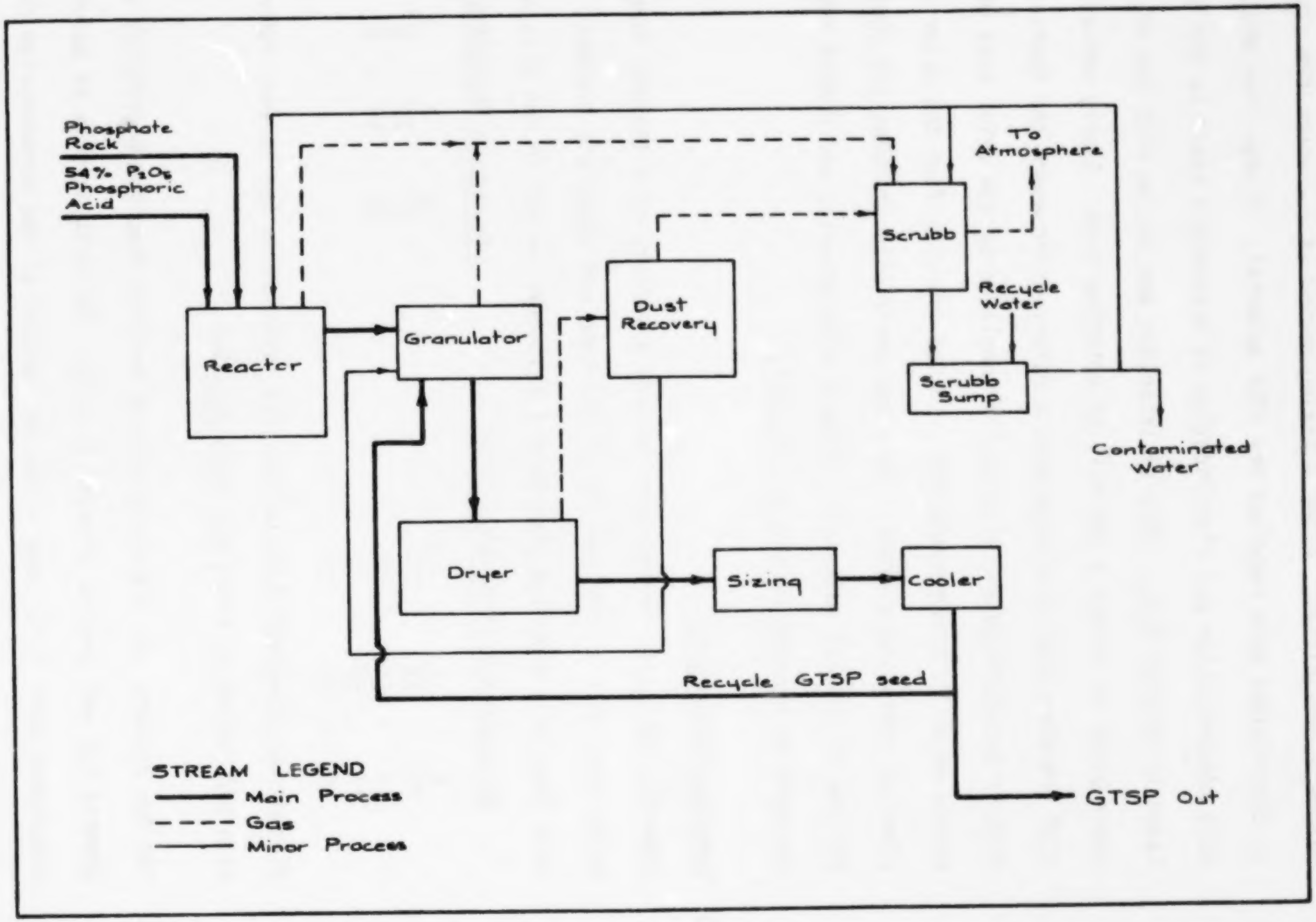


Figure 2.8 Granulated Triple Superphosphate (EPA 440/1-74-011a)

the chemical reaction to proceed appreciably further toward completion before it solidifies. After a mixing period of 1-2 hours the slurry is distributed onto recycled dry GTSP material. Sludge from phosphoric acid concentration and clarification is frequently added to the granulator to recover P_2O_5. This distribution and mixing with the dry GTSP takes place in either a pug mill or rotating drum. Slurry wetted GTSP granules then discharge onto a rotary drier where the chemical reaction is accelerated and essentially completed by the drier heat while excess water is being evaporated. Dried granules from the drier are sized on vibrating screens. Over and under-size granules are separated for use as recycle material. Product size granules are cooled and conveyed to storage or shipped directly.

2.1.15 Ammonium Phosphates

Ammonium phosphate fertilizers include a variety of different formulations which vary only in the amounts of nitrogen and phosphate present. The most important ammonium phosphate fertilizers in use in the U.S. are:

Monoammonium Phosphates (MAP)

N	P	K
11	48	0
13	52	0
11	55	0
16	20	0

Diammonium Phosphates (DAP)

N	P	K
16	48	0
18	46	0

Diammonium phosphate formulations are produced in the largest tonnages with DPA (18-46-0) being the most dominant.

The two primary raw materials used to produce ammonium phosphates are ammonia and wet process phosphoric acid. Sulfuric acid is of secondary importance when it is used in the production of the monoammonium phosphate grade 16-20-0. As mentioned above, the various grades differ only in the amounts of nitrogen and phosphate present. It is primarily the nitrogen that varies and this is accomplished by controlling the degree of ammoniation during neutralization of the phosphoric acid. The chemical reactions involved are indicated by the following equations:

$$\underset{\text{Phosphoric Acid}}{H_3PO_4} + \underset{\text{Ammonia}}{NH_3} \longrightarrow \underset{\text{Monoammonium Phosphate}}{NH_4H_2PO_4} \qquad (2.13)$$

$$\underset{\text{Sulfuric Acid}}{{}^*H_2SO_4} + \underset{\text{Ammonia}}{2NH_3} \longrightarrow \underset{\text{Ammonium Sulfate}}{(NH_4)_2SO_4} \qquad (2.14)$$

*This reaction occurs only in the production of 16-20-0 and occurs concurrently with the monoammonium phosphate reaction.

The processing steps are outlined in Figure 2.9. Ammonia, either gaseous or liquid, is reacted with 30-40% phosphoric acid in a cylindrical ammoniator vessel which may or may not have mechanical agitation. The resultant slurry is distributed onto dry recycled material which is used to control moisture. Distribution and mixing takes place in either a pug mill or rotating drum where granules are formed continuously. Wetted granules then discharge into a rotary drier where the excess water is evaporated. Dried granules are classified and a fraction separated for use as recycle material. Product size granules are cooled and conveyed to storage or shipped directly.

The wet scrubbers are the only significant sources of wastewater from the process. When ammonium phosphate is produced at an integrated fertilizer complex the scrubber will most likely utilize the gypsum pond water.

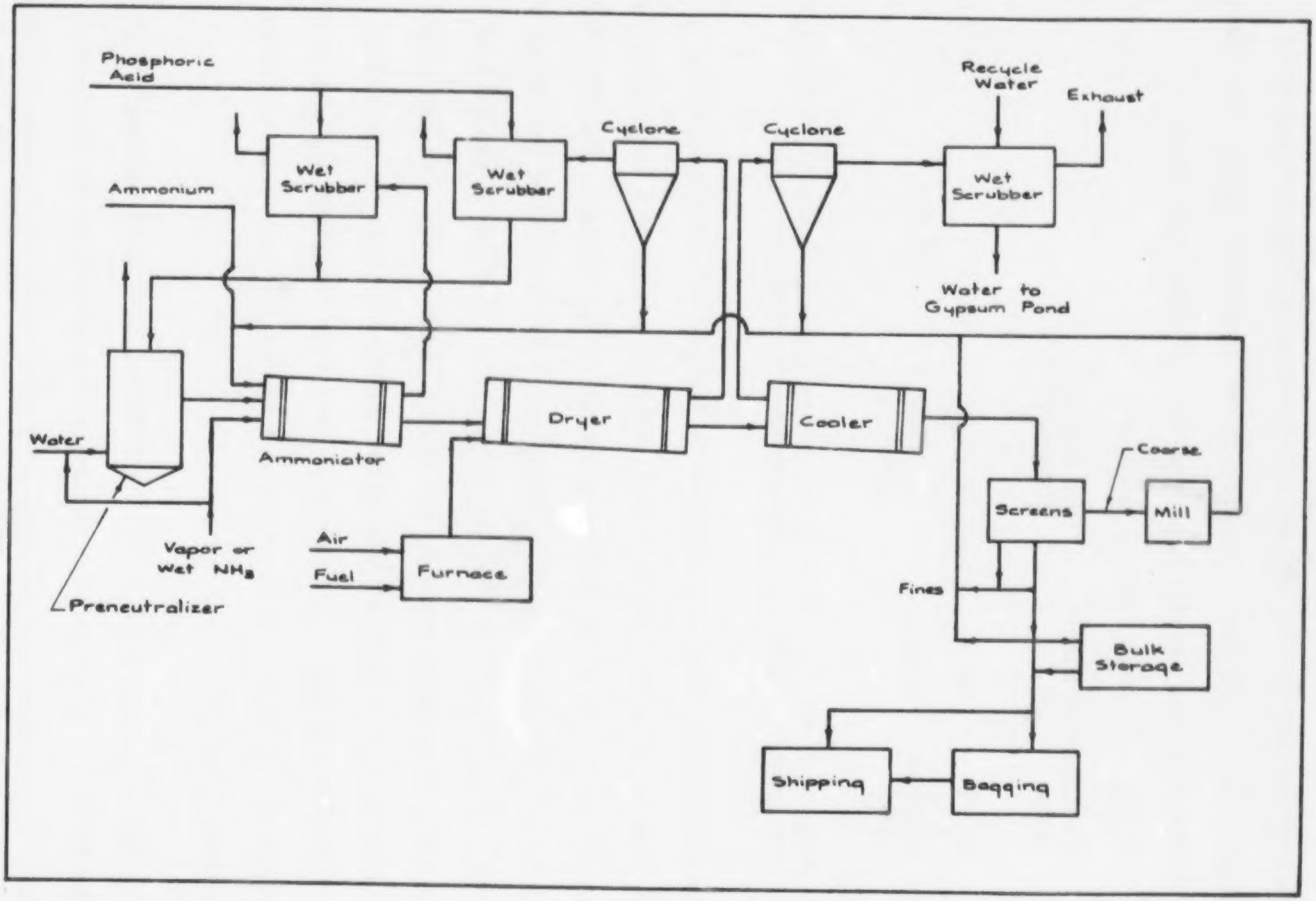


Figure 2.9 Diammonium Phosphate Process Schematic (Shrieve, p 227)

2.1.16 Defluorinated Phosphate Rock

Phosphate rock is used as an animal feed supplement in many regions, however, fluoride contaminants must be removed from the material prior to this use. A rotary kiln or a fluidized bed reactor utilizing sodium or silica fluxes are the most common processes in use. If this product is made in a phosphoric acid complex, gypsum pond water would be used for wet scrubber water (Figure 2.10).

The fluorapatite type of phosphate rock is the primary raw material. Phosphate content of the rock is typically 35% P_2O_5. Other raw materials used in lesser amounts but very critical to the process include sodium containing reagents, wet process phosphoric acid and silica. The quantity, point of addition of these materials to the process, and how they are mixed with the phosphate rock constitute some of the know-how involved to realize a workable process and a consistent product quality. These raw materials are added in specific quantitites or ratios dependent upon the feed phosphate rock analysis.

The sodium containing reagent is commonly soda ash (sodium carbonate) which has a 58% Na_2O content or a 98% Na_2CO_3 content. The wet phosphoric acid reagent concentration used is 45-54% P_2O_5. Silica addition is in the form of sand and is dependent on the silica present in the basic phosphate rock feed. The point of addition and the material mixing techniques (either as a physical mixture or agglomerated into nodular form) are trade secrets. The above described mixture or charge is then fed into either a rotary kiln or a fluid bed reactor. In the case of a fluid bed reactor, it is desirable that the charge be nodular and dried prior to being

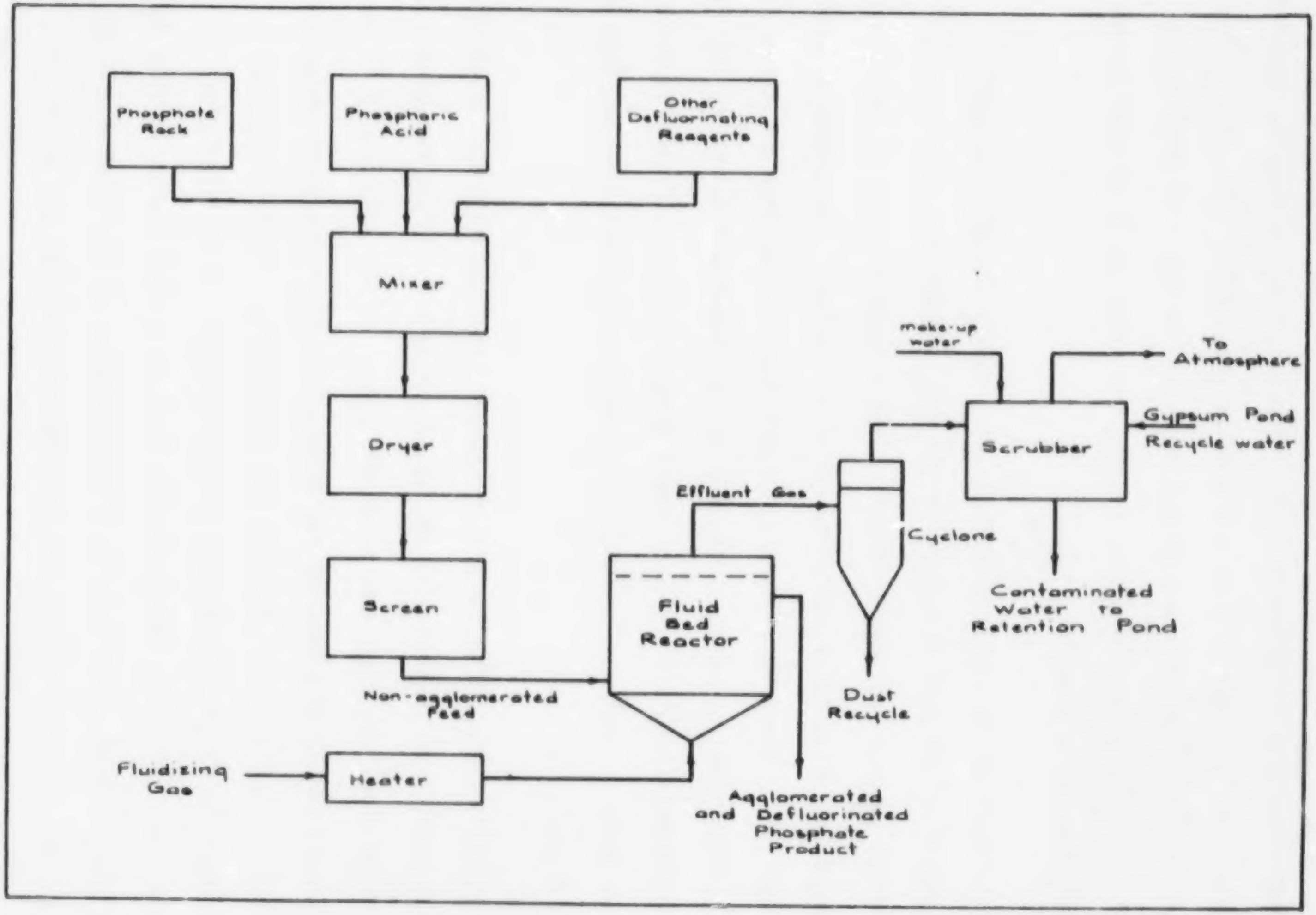


Figure 2.10 Defluorinated Phosphate Rock - Fluid Bed Process Schematic (EPA 440/1-75/043)

fed into the reactor. This is to permit the fluid bed to classify different sized particles and to minimize loss in the exhaust gas. Temperature control and retention time are the process variables which require close control in both the kiln and fluid bed reactor. Reaction temperatures are maintained in the 1200-1370°C (2200-2700°F) range with the rotary kiln requiring the upper portion of the range. Retention time ranges from 30 to 90 minutes with the fluid bed reactor generally requiring the lesser time.

The state of the charge in the kiln or fluid bed reactor is highly dependent upon the ratio of the raw materials added to the phosphate rock. This ratio determines whether the fluorine is evolved in a minimal time period and in sufficient quantity, and/or whether the charge fuses into an unmanageable mass that solidifies in the unit. Another critical factor in these units is that water vapor content be maintained at a sufficiently high percentage to effect the required fluorine evolution. An equation representative of the chemical reaction and fluorine release in the kilns and fluid bed reactors is:

$$\underset{\text{Phosphate rock}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{Water}}{H_2O} + \underset{\text{Silica}}{SiO_2} \longrightarrow \underset{\text{Tricalcium Phosphate}}{3Ca_3(PO_4)_2} + \underset{\text{Calcium Silicate}}{CaSiO_3} + \underset{\text{Hydrogen Fluoride}}{2HF} \quad (2.15)$$

From the kiln or fluid bed reactor, the defluorinated product is quickly quenched with air or water. This is necessary to maintain the product in the alpha rather than beta tricalcium phosphate form. The alpha form is the high solubility material most desirable in the final product. From this point the product is crushed and sized for storage or shipment. (EPA 440/1-75/043).

2.1.17 Fluosilicic Acid Recovery

Vapors from the evaporator/concentrators used to produce 54%-76% P_2O_5 acid are by far the most attractive source of by-product fluorides from wet-process phosphoric acid and other fertilizer process operations. Estimates of fluoride evolution from this process operation range as high as 80% of the total fluoride content of the input phosphate rock. The resultant high concentrations of fluoride vapors make recovery of the fluosilicic acid economically as well as technically feasible.

Significant quantities of fluoride are also evolved from other process operations that are found in most phosphoric acid/fertilizer complexes, including acidulation and filtration of phosphate rock to produce phosphoric acid and acidulation of phosphate rock, curing, cutting, and storage processes used to produce normal and triple superphosphate. These fluorides, however, are not recovered because of their relatively low concentration in the gas stream and resultant high costs and technical difficulties.

Fluosilicic acid recovery equipment is utilized primarily with the vacuum type evaporator/concentrator. A typical unit is shown in Figure 2.2 as it would be used in the dihydrate process. It would also be applicable to the vacuum process for defluorinated superphosphoric acid production depicted in Figure 2.4.

2.2 CHARACTERIZATION OF SOURCES OF GYPSUM POND FLUORIDES

2.2.1 Drying and Grinding of Phosphate Rock

This operation does not generate any wastewaters.

2.2.2 Calcining (Defluorinated Rock)

This process operation (Figure 2.10) uses wet scrubbers to control gaseous emissions. Gypsum pond water is used in the scrubber if available. Up to 65% of the fluoride originally in the rock can be evolved below fusion temperature. At the fusion temperature (2500° to 2700°F) 87-90% of the fluorine can be removed (Teller). A typical water flow rate through the scrubber is 11,000 gal/ton rock (EPA 440/1-75/043). Gaseous concentrations may range from 7.7-30.8 gr/cf.

2.2.3 Normal Superphosphate

Acidulation of phosphate rock with H_2SO_4 evolves 11 to 42% of the fluorine in the rock. Reaction temperatures are low (200-400°F rise) and SiF_4 is the major compound evolved (Teller). Range of concentration over the den is 3.1-77.1 gr/cf.

2.2.4 Phosphoric Acid - Digestion and Filtration

In the production of wet-process phosphoric acid, both the type of rock and the processing techniques affect the quantity of gaseous fluorides evolved. Typical fluorine contents of the rock are as follows:

Table 2.6 Fluoride Content of Phosphate Rock
(Teller, p. 745)

Source	%P_2O_5	%F
Florida land pebble	30.5-32.6	3.3-3.9
Tennessee	27.9-32.4	2.9-3.7
Western U.S.	27.5-32.5	2.9-3.8
Morocco	35.1	4.2
Tunis	27.6	3.5
Christmas Island	39.5	1.3
Curacao Island	38.6	6.7
Nauru Island	38.9	2.6
USSR (Kola)	40.3	3.3
Ocean Island	40.3	3.0

In the reaction of the rock with sulfuric acid to produce phosphoric acid plus gypsum, the fluorine originally present in the rock is distributed in the precipitated gypsum, the phosphoric acid, and the exhaust gas (as SiF_4). The relative quantities of fluorine in the final products depend on the type of rock and the operating conditions. The main factors appear to be:

1) the quantity of sodium or potassium salts present (which will precipitate insoluble fluoride compounts);
2) the reaction temperature at which digestion occurs (increasing temperature results in increasing gaseous emission);
3) the concentration of the product phosphoric acid;
4) acid:rock ratio
5) quantity of silica, aluminum and iron in the rock.

The effect of source and type of rock on distribution of the fluorine in the dihydrate digestion process is as follows:

Table 2.7 Distribution of Fluoride in Dihydrate Process (Teller, p. 745)

Rock Source	Distribution of fluoride, % of total		
	In acid	In gypsum	In exhaust gas
Nauru	23	75	2
Kola	73	15	12
Florida	52	45	3
Morocco	50	47	3

The effect of the type of process on fluoride concentration in the off-gases from digestion depends on the quantity of diluent air. Digestion of Florida rock will result in gaseous emission of 2 to 8 lb. of fluoride per ton of rock fed to the reactor when 26 to 30% P_2O_5 acid is produced. With air cooling of the reactor, the fluoride concentration in the off-gases will range from 0.6-1.2 gr/cf. If vacuum flash cooling is used, the concentration will range from 3.1 to 7.7 gr of F^- per cubic foot. A small amount of solids, less then 0.8 gr/cf, is present in the effluent gas.

During acid filtration small amounts of SiF_4 are released which must be vented and scrubbed to meet the new air emission standards. These gases, carrying 0.15 to 0.45 gr of F^- per foot, are usually vented to the digestor-scrubber.

Equipment is available to reclaim the fluoride as H_2SiF_6 from the digestion process exhaust gas, however, the economic and the operational feasibility is marginal due to the relatively low amounts of fluoride present.

2.2.5 Concentration and Defluorination of Phosphoric Acid

Concentration of 32% to 54% P_2O_5 acid has been estimated to evolve 25% (Teller).

35% (Fox), 42% (Sanders), and 80% (Forster) of the total fluoride input to a wet-process acid plant. These authors are in agreement, however, that the proper use of recovery units (such as in Figure 2.2) will permit recovery of up to 90% of this fluoride as by-product H_2SiF_6. The unrecovered fluoride is discharged to the gypsum pond.

2.2.6 Triple Superphosphate ROP

Fluorides are evolved in the ROP process in two steps (Figure 2.7). The first stage is in the mixing cone, the transfer den, and the cutters where 31-33% of the total fluoride available in the feed is evolved. The second is during the 2-4 week curing and storage period when 2.0-2.8% of the original fluoride is released as SiF_4. Teller also estimates that 67 to 74% of the fluoride is retained in the product ROP-TSP.

Under ideal operating conditions wet scrubbers will capture 99+% of evolved fluorides and transfer them to the gypsum pond cycle.

2.2.7 Granular Triple Superphosphate

Significant gaseous fluoride evolution also occurs in the manufacture of granular triple superphosphate (Figure 2.8) along with production of dust. The major gaseous evolution occurs in the reactor-dryer system but additional evolution occurs in the product cooler and in the storage building.

The slurry resulting from reaction of the rock and 40% P_2O_5 acid is sprayed on recycled product and dried. The fluoride evolution during this operation is high, as much as 25 lb/ton of P_2O_5. The gas effluent essentially is SiF_4, inasmuch as any HF formed immediately attacks the rock to form H_3PO_4 and H_2SiF_6. The concentration of fluoride in the dryer effluent ranges from

0.9 to 1.5 gr/cf in a gas flow of 60 to 200 ft^3/min/daily ton of P_2O_5 produced. (11 to 62 lbs F/ton P_2O_5). The particulate loading of this stream is approximately 231 gr/cf. The effluent from the cooler contains between 0.23-0.46 gr/cf of gaseous fluoride in the form of SiF_4, and also has a particulate loading of approximately 231 gr/cf. Granular TSP will also evolve 2.0-2.8% of the original fluoride content as SiF_4 while in storage for a four week period. Wet scrubber water recirculated from the gypsum pond will capture 99+% of the evolved fluoride and transport it to the gypsum pond.

2.2.8 Ammonium Phosphate

Gaseous fluorides are evolved from the ammonization of phosphoric acid, the dryer, the cooler, and storage. Emissions of fluorides are relatively low due to the fact that the feed phosphoric acid has already evolved about 75% of the fluoride originally held in the rock. Calculations based on observations by Huffstutler indicate that about 33% of the remaining fluoride in the phosphoric acid is evolved in this process.

2.2.9 Gypsum Pond and Phosphoric Acid Complex Fluoride Mass Balance

Typical fluoride distributions in the manufacture of wet process phosphoric acid as derived from the literature are presented in Tables 2.8, 2.9 and 2.10.

Table 2.8 Fluoride Distribution in Phosphoric Acid Production (Sanders, p. 765

Processing stage	% total fluoride in phosphate rock	Lb of fluoride per ton of P_2O_5
Production of filter acid		
Phosphate rock (32.57% P_2O_5, 3.89% F)	100	239
Vapors from reactor slurry	5.5	13
Gypsum filter cake	27.8	66
30% P_2O_5 filter acid	66.7	160
Concentration of filter acid		
Vapors from concentrators	41.9	100
54% P_2O_5 concentrated acid	24.8	60

Table 2.9 Fluoride Distribution in Phosphoric Acid Production (Fox)

Processing stage	% total fluoride in phosphate rock
Gypsum filter cake	46.2
Concentrated acid	13.3
Volatilized, total	40.5
In rock digestion	5.2
In acid concentration	35.3

Table 2.10 Distribution of Fluorides from Florida Phosphate Rock (Huffstutler, p. 728)

Input rock	To H_3PO_4 lf/day F^-	% F^- input	To gypsum lb/day F^-	% F^- input	To pond water lb/day F^-	% F^- input	To atmosphere lb/day F^-	% F^- input
73,600	21,500	29	30,000	41	21,200	29	12	0.016
116,300	28,000	24	39,000	34	48,500	42	30	0.026
355,600	105,900	30	75,100	21	174,600	49	24	0.007

A fluoride mass balance and a gypsum pond recycle flow balance for a phosphate fertilizer complex has been synthesized based on available information (Figure 2.11). A phosphoric acid plant which produces 32% P_2O_5 by the dihydrate process 70 BPL Florida phosphate rock (32.57% P_2O_5, 3.89% F^-) and concentrates it to 54% P_2O_5 in a two stage forced circulation vacuum

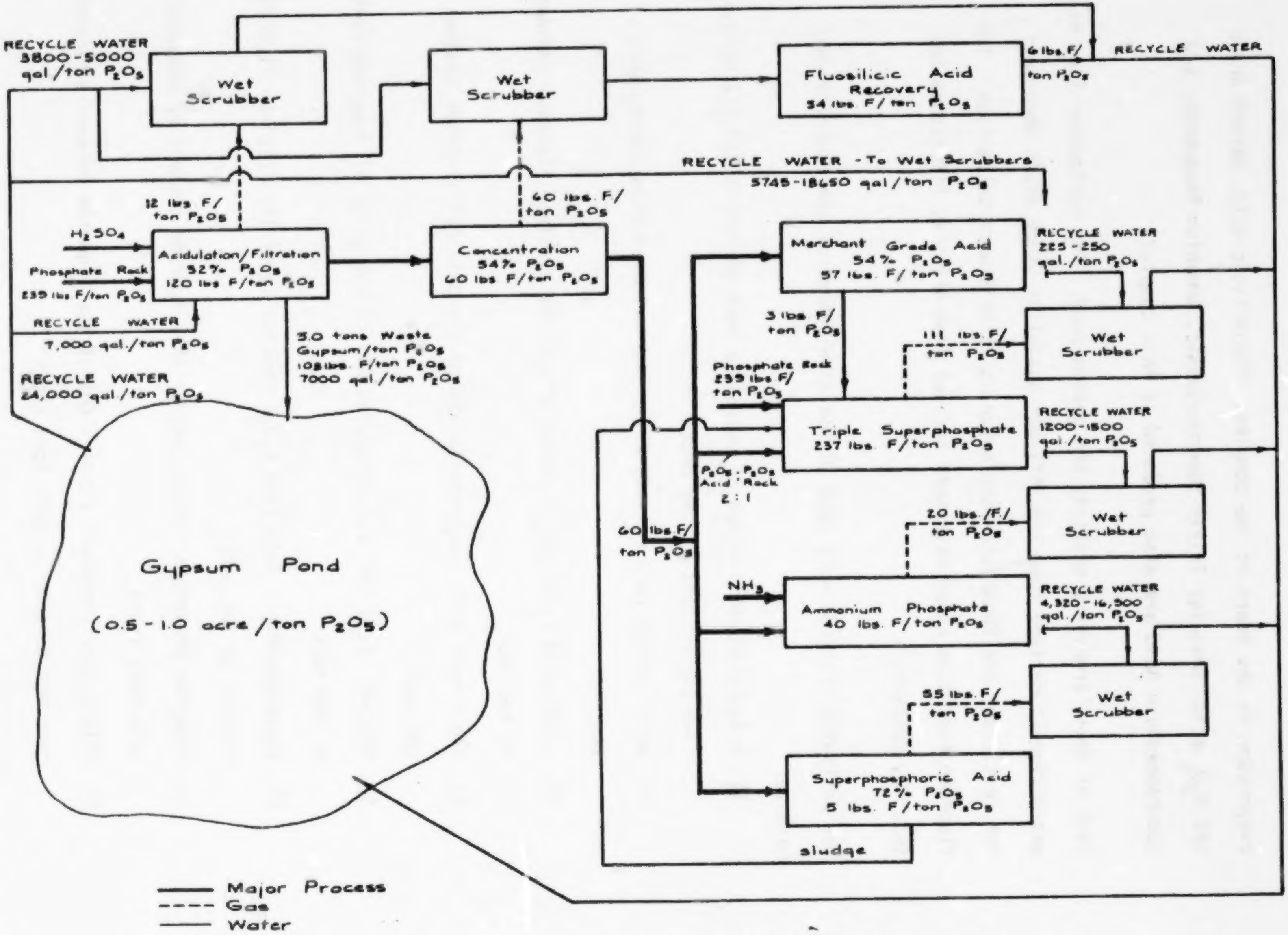

RECYCLE WATER 3800-5000 gal/ton P_2O_5
Wet Scrubber
Wet Scrubber
Fluosilicic Acid Recovery 54 lbs F/ton P_2O_5
6 lbs. F/ton P_2O_5
RECYCLE WATER
RECYCLE WATER - To Wet Scrubbers 5745-18650 gal/ton P_2O_5
12 lbs. F/ton P_2O_5
60 lbs. F/ton P_2O_5
H_2SO_4
Phosphate Rock 239 lbs F/ton P_2O_5
Acidulation/Filtration 32% P_2O_5 120 lbs. F/ton P_2O_5
Concentration 54% P_2O_5 60 lbs F/ton P_2O_5
RECYCLE WATER 7,000 gal./ton P_2O_5
RECYCLE WATER 24,000 gal/ton P_2O_5
3.0 tons Waste Gypsum/ton P_2O_5 108 lbs. F/ton P_2O_5 7000 gal/ton P_2O_5
Merchant Grade Acid 54% P_2O_5 57 lbs. F/ton P_2O_5
RECYCLE WATER 225-250 gal./ton P_2O_5
3 lbs. F/ton P_2O_5
111 lbs. F/ton P_2O_5
Wet Scrubber
Phosphate Rock 239 lbs F/ton P_2O_5
Triple Superphosphate 237 lbs. F/ton P_2O_5
RECYCLE WATER 1200-1800 gal./ton P_2O_5
P_2O_5 : P_2O_5 Acid Rock 2 : 1
60 lbs. F/ton P_2O_5
20 lbs. F/ton P_2O_5
Wet Scrubber
Gypsum Pond
(0.5 - 1.0 acre/ton P_2O_5)
NH_3
Ammonium Phosphate 40 lbs. F/ton P_2O_5
RECYCLE WATER 4,320-16,300 gal./ton P_2O_5
55 lbs. F/ton P_2O_5
Wet Scrubber
Superphosphoric Acid 72% P_2O_5 5 lbs. F/ton P_2O_5
sludge
Major Process
Gas
Water

Figure 2.11 Phosphate Fertilizer Complex - Fluoride and Water Balance

evaporator is the heart of the complex. Fluosilicic acid, Market Grade 54% P_2O_5 acid, Granular Triple Superphosphate, Ammonium Phosphate, and Superphosphate Acid are also produced at this complex.

Each of these processes utilizes the gypsum pond. The wastewater flow data was primarily derived from EPA Effluent Guideline Study draft documents for Fertilizer and Phosphate Manufacturing Point Source Categories. The fluoride evolution rates have been derived from existing literature and industry contacts.

The following criteria were used in the development of the fluoride mass balance:

1) Acidulation/Filtration of phosphate rock evolves 5% of the original fluoride content of the rock
2) Waste gypsum cake retains 45% of the original fluoride content of the rock
3) Black acid (32% P_2O_5) retains 50% of the original fluoride content of the rock
4) Black acid (54% P_2O_5)retains 25% of the original fluoride content of the rock
5) Merchant acid (54% P_2O_5) retains 24% of the original fluoride content of the rock
6) Superphosphoric Acid (72% P_2O_5) retains 2% of the original fluoride content of the rock
7) Ammonium phosphate retains 66% of the fluoride content of phosphoric acid feed stock.
8) Triple superphosphate retains 66% of the fluoride content of phosphate rock and phosphoric acid feed stock

9) Fluosilicic acid recover reclaims 90% of fluoride evolved from evaporation/concentration.

2.2.10 Gypsum Pond and Phosphoric Acid Complex Water Balance

Contaminated gypsum pond water is used in all process equipment in the phosphate subcategory except sulfuric acid manufacturing and rock grinding. The water requirements of such major water using equipment as barometric condensers, gypsum sluicing, gas scrubbing equipment, and heat exchangers are all supplied by contaminated water. Each time the water is reused, the contaminant level is increased. However, build-up rates of fluoride are not documented. While this contaminated water is a major process effluent, it is not routinely discharged from the gypsum pond complex. The following tables (2.11 and 2.12) list ranges of contaminated water usage for each contact and non-contact process.

Table 2.11 Phosphate Complex Water Usage (EPA 440/1-74-011-a)

Process	Gypsum Pond Recycle gal/ton P_2O_5	Fresh Water Make-up
Sulfuric Acid	None	15-20
Rock Grinding	None	None
Wet Process Phosphoric Acid		
Process Water	3800-5000	None
Sluice Water	7000-11000	None
NPK Process-Nitric Acid Acidulation	240-540	None
Phosphoric Acid Concentration	550-570	0.2-0.4
Phosphoric Acid Clarification	225-250	None
Normal Superphosphate	225-250	None
Triple Superphosphate	158-250	None
Ammonium Phosphate	1200-1500	None
Rock Calcining	11000	None
Defluorinated Phosphonic Acid		
Vacuum Evaporation	16900	
Submerged Combustion	4300	

Table 2.12 indicates the water balance around a plant using 94% H_2SO_4. without dilution, with vacuum cooling and evaporation of the product acid to 54% P_2O_5 by stage-wise evaporation. A cooling water temperature of 90° F^- is assumed. These conditions represent a plant located in the southern United States or in areas of equivalent climatic conditions.

Table 2.12 Water Requirements for Phosphoric Acid Production (Lutz, p. 195)

	U.S. gal/short ton of P_2O_5
Contaminated water	
Filter wash and repulp	7,000
Vacuum cooler condensers	7,500
Evaporator condensers	14,000
Scrubber water	1,000
Fresh water	
Cooling water for sulfuric dilution cooler	5,000
Vacuum pump water	300
Process water for H_2SO_4 dilution	300
Sanitary and miscellaneous usage	300

It is immediately obvious that there are some discrepancies between flow ranges assigned to scrubbers and the order of magnitude of fluoride loadings on those same scrubbers in Figure 2.11. For example, an estimated 111 lb F^-/ton P_2O_5 evolves from the triple superphosphate process, yet only 225-250 gal of water/ton P_2O_5 is allocated to that process by the Effluent Guidelines Contractor. However, for the acidulation/filtration process 3800-5000 gal/ton P_2O_5 is allotted to remove a mere 12-16F^-/ton P_2O_5. At this time there are no better figures available to explain or pinpoint the cause for such discrepancies. The numbers which have been used must be considered to be order-of-magnitude.

2.3 SECTION 2 CONCLUSIONS

1) The dihydrate process is the most commonly used wet process for the manufacture of phosphoric acid in the United States. It is common practice within the phosphate industry to also manufacture one or more phosphate based fertilizers in the phosphoric acid complex.

2) The existence of the gypsum pond is dependent on the use of the dihydrate wet process to manufacture phosphoric acid. Secondary fertilizer manufacturing processes within a fertilizer complex then utilize the gypsum pond water in several contact and non-contact process operations.

3) Under normal operating conditions the evolution of fluorides from the various unit processes will be in order-of-magnitude agreement with generation rates developed for the fluoride mass balance sheet (Figure 2.11). However, process upsets - such as wasting of acidulated rock to restore the proper rock:acid ratio - may result in short-term increases in fluoride loading to the gypsum pond which have not been characterized.

4) General operating parameters which affect fluoride loading on the gypsum pond for all phosphoric acid and phosphate fertilizer unit processes are as follows:
   a) Product specifications
   b) Raw material specifications
   c) Temperature of the reactions
   d) Acid concentrations
   e) Fluoride emission standards
   f) Fluoride recovery (if any).

A major operational parameter in phosphoric acid production is control of the crystaline form of calcium sulfate formed in the acidulation/ filtration process.

5) Fluosilic acid recovery on the evaporator/concentrator has been demonstrated to remove approximately 23% of input rock fluorides from the waste water which is discharged to the gypsum pond.

3.0 GYPSUM POND CHEMISTRY

This section is to evaluate the potential for airborne fluorine emission from gypsum ponds. This evaluation necessitates a fundamental understanding of the chemical interactions involving fluorine in the gypsum pond environment. A theoretical and literature-based approach to this problem is a first step in evaluating the potential for airborne emissions.

3.1 SOURCE OF FLUORINE IN GYPSUM PONDS

Figure 2.11 illustrates the sources of fluorine in a gypsum pond associated with a phosphate rock processing facility. There are two sources: fluorine released from the rock matrix during the acidulation process and fluorine recovered by wet scrubbers from gaseous emissions at various points in the process. Fluorine is released in the production of phosphoric acid by the wet-process during acidification of the fluorapatite ore with sulfuric acid:

$$Ca_{10}(PO_4)_6F_2(s) + 10H_2SO_4(aq) + 10nH_2O(l) \longrightarrow 10CaSO_4\ nH_2O(s) + 6H_3PO_4(aq) + 2HF(aq) \qquad (3.1)$$

where n may equal 0, 1/2, or 2 depending on the form of the hydrated calcium sulfate ($CaSO_4$). Some of the fluoride present in the phosphate rock as calcium fluoride (CaF_2) will react with phosphoric acid (H_3PO_4) and sulfuric acid to form hydrofluoric acid (HF):

$$CaF_2(s) + 2H_3PO_4(aq) \longrightarrow Ca(H_2PO_4)_2(aq) + 2HF\ (aq) \qquad (3.2)$$

$$CaF_2(s) + H_2SO_4(aq) + H_2O(s) \longrightarrow CaSO_4 \cdot 2H_2O(s) + 2HF(aq) \qquad (3.3)$$

The HF will then react with silicate (SiO_2) released from the rock matrix to form fluosilicic acid:

Table 3.1 Major cation and anion concentrations in gypsum pond water. After ESE, 1974.

Cations	concentration (mg/l)	concentration (M)
Ca^{++}	2000	0.05
Na^{+}	1600	0.07
Al^{3+}	500	0.018
Fe^{3+}	300	0.005
Mg^{++}	240	0.01
K^{+}	200	0.005
H^{+}	pH = 1.4	0.04
Anions		
$F^{\ominus}$	8000	0.42
$SO_4^{=}$	4800	0.05
Cl^{-}	200	0.006
$H_2PO_4^{-}$	1000	0.02

$$SiO_2(s) + 6HF(aq) \longrightarrow H_2SiF_6(aq) + 2H_2O\cdot(\ell) \qquad (3.4)$$

As a result of the elevated temperatures encountered in the acidulation, concentration and other processing steps, a portion of the HF released from the rock matrix is volatilized as hydrogen fluoride. Fluosilicic acid (H_2SiF_6) is also dissociated into hydrogen fluoride and silicon tetrafluoride (SiF_4) at elevated temperatures:

$$H_2SiF_6(s) \xrightarrow{\Delta} SiF_4(g) + 2HF\cdot(g) \qquad (3.5)$$

Hydrogen fluoride and SiF_4 are prevented from escaping from the facility into the atmosphere in large quantities by the use of wet scrubbers employing recycled gypsum pond water as the scrubbing medium. In the scrubbers, hydrogen fluoride and SiF_4 are removed from the air forming H_2SiF_6:

$$3SiF_4(g) + 2H_2O(\ell) \longrightarrow 2H_2SiF_6(aq) + SiO_2(s) \qquad (3.6)$$

$$SiO_2(s) + 6HF(g) \longrightarrow H_2SiF_6(aq) + 2H_2O\cdot(\ell) \qquad (3.7)$$

If it is assumed that there exists a sufficient excess of silicate in the rock, and this is not an unreasonable assumption for most natural minerals; then the net result of all of the above reactions is that most fluorine enters the gypsum pond in the form of H_2SiF_6 and possibly CaF_2. Smaller quantities of HF(aq), Na_2SiF_6 and K_2SiF_6 will likely be present as well. All chemical reactions result in an equilibrium among the reactants and the products. Each of the above equilibria, however, are balanced far in the direction shown.

An attempt was made to evaluate the magnitude of possible airborne fluorine emissions from the gypsum pond by mass balance calculations of the fluorine entering the pond and leaving the pond. A mass balance is, however, impractical as a result of the orders of magnitude involved. To illustrate this, a 1000 ton per day P_2O_5 plant using ore containing 3.8 percent fluorine would deliver approximately 140 tons of fluorine to the gypsum pond per day. If 40 percent of that fluorine existed as CaF_2, the daily flow of soluble fluoride would be as large as 84 tons. Assuming a large pond (300 acres) evolving HF at the rate of 4.7 lb/acre/day (the highest rate suggested in the available literature, King, 1969), 1,410 lbs of fluoride would be emitted to the air each day. This emission rate represents only 0.83 percent of the 84 tons entering the pond each day. Given the variability of pond influent composition and the uncertainties inherent in composite wastewater sampling and analysis, an airborne emission rate of 4.7 lb/acre would be impossible to document by mass balance calculations even with a very large number of samples. The problem would be further complicated should the actual emission rate be less than 4.7 lb/acre or the pond smaller than 300 acres.

3.2 CHEMICAL ENVIRONMENTAL WITHIN THE GYPSUM POND

Gypsum pond water is a complex mixture of various charged and uncharged chemical species. Some of the major cations and anions present are listed in Table 3.1 along with the approximate analyzed concentrations. Additional minor elements such as Mn, Cu, Cr, Zn, Ba, U, and Sr elements are also present in smaller quantities. H_3PO_4, SiO_2, H_2SiF_6, CaF_2 and a large number of complexed chemical species will be present. Fluorine, designated F^- in Table 3.1, will occur as the fluoride ion F^-, as H_2SiF_6, $HF_{(aq)}$, SiF_4, HF_2^- and complexed with metals such as FeF_3, AlF^{++}, AlF_2^+, AlF_3, AlF_4^-, etc.

Gypsum pond waters are of high ionic strength ($I \approx 1$ mole/l) as a result of the large concentrations of charged species present. Ionic strength will affect each of the equilibrium constants used in this evaluation to a considerable extent. The present state of knowledge of gypsum pond chemistry is, however, not sufficient to warrant the complication of the problem at this point. In general, high ionic strenth will tend to oppose those reactions that contribute multivalent ions to solution. Equilibria would tend to be more balanced toward the uncharged or low-charged products than basic equilibrium theory suggests.

The observed pH of gypsum pond waters is 1.5 to 2.0. At this pH, weak acids will exist largely in the undissociated (protonated) state. Eighty percent of the phosphate present should exist as H_3PO_4 while approximately 20 percent is $H_2PO_4^-$. H_2SiF_6 and HF will both exist predominantly in the undissociated condition.

A titration curve for a typical gypsum pond water is presented in Figure 3.1. From that titration curve, the buffer capacity ($B = dC_B/dpH$, Stumm and Morgan, 1970) of the solution as a function of pH has been calculated and is illustrated in Figure 3.2. It is apparent that the system is highly buffered both initially and in the vicinity of pH 7. The higher of the two buffered pH regions appears to coincide with the $HPO_4^{2-}/H_2PO_4^-$ buffering maximum. The engineering and economic significance of the buffering capacity figure is obvious. Large amounts of lime ($Ca(OH)_2$) are required to raise the pH initially to 3 and from 6 to 8, relative to the amount needed to raise the pH of the pond water from 3 to 6.

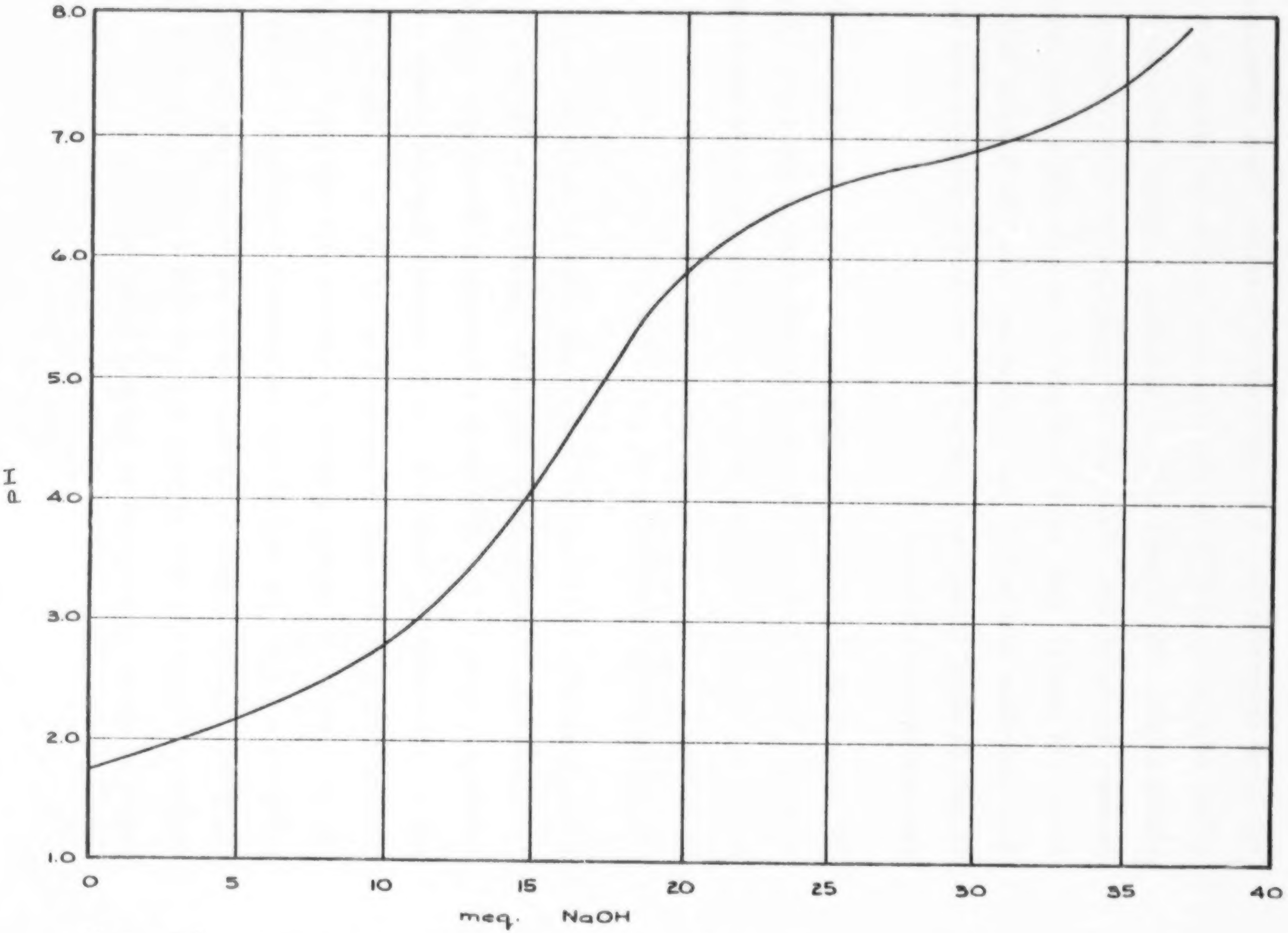


Figure 3.1 - Titration of Gypsum Pond Water with 1 N NaOH.

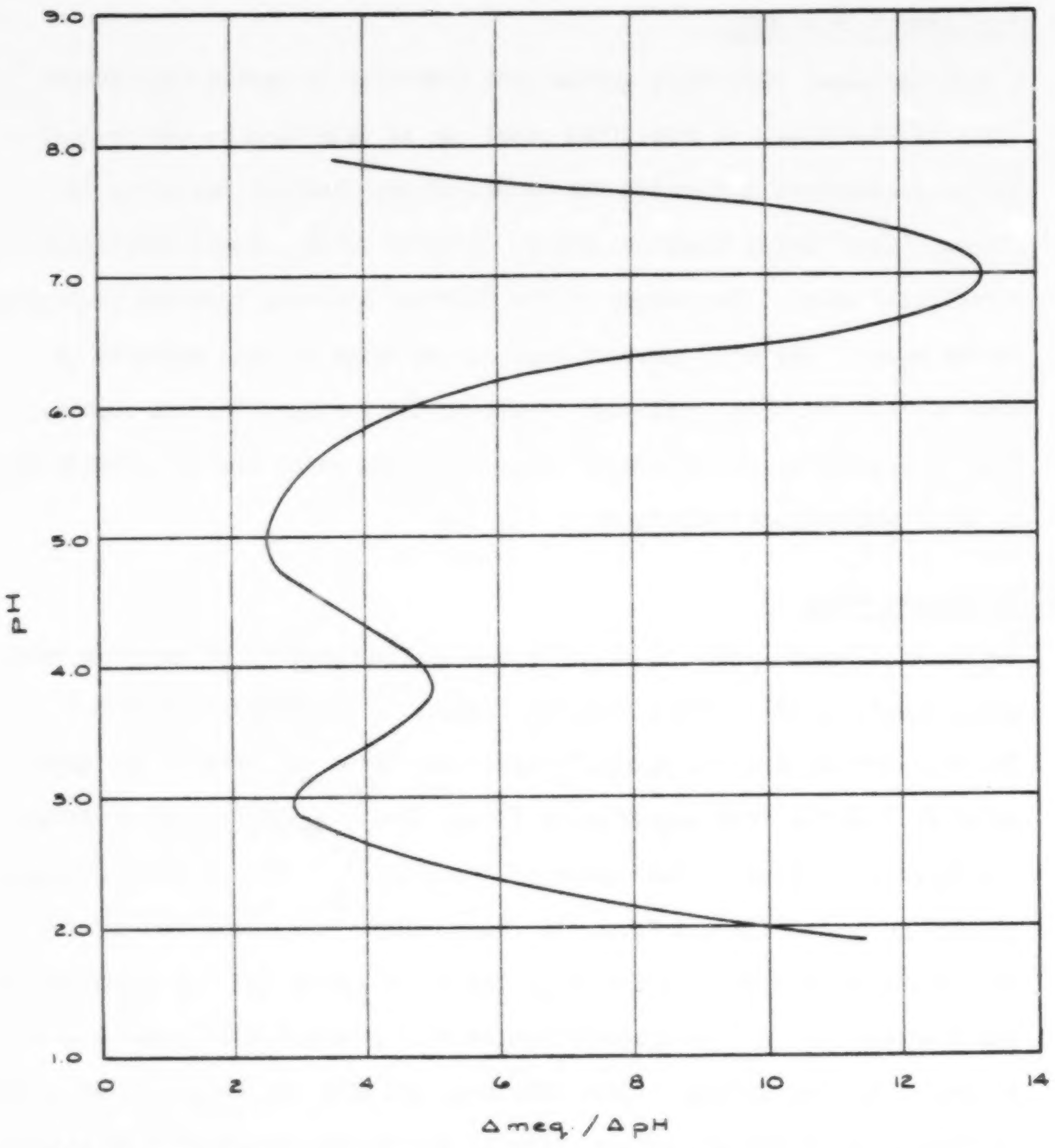


Figure 3.2 - Buffer Capacity of Gypsum-Pond Water.

3.3 DEVELOPMENT OF A MODEL

A detailed model describing gypsum pond chemistry is beyond the current state of knowledge. A simplified model can be developed by making qualitative assumptions concerning the nature of the chemical reactions involved. Equilibrium equations alone, while of value, cannot constitute a realistic model. The nature of the chemical kinetics involved is crucial to the model. The only approach that can be taken at this point is to consider all the major reactions involving the various fluoride species, then to systematically eliminate those reactions which are not considered to be of predominant importance.

3.3.1 An Initial Model

The initial model, which is actually a pictorial summary of possible reactions involving the various fluoride species is presented in Figure 3.3. The equilibrium that has generally been considered dominant in the generation of fluoride from gypsum ponds (King, 1969), $H_2SiF_6(aq) \rightleftarrows 2HF(aq) + SiF_4(aq)$, is shown in the center of the diagram. This reaction proceeds through several different routes as shown. Other reactions include the precipitation of fluosilicic acid as the Na or K salt and the formation of the fluoride ion, F^-, by dissociation of HF. Fluoride will combine with Al and Fe to form soluble fluoro complexes and with Ca, Mg and other cations to form salts of low solubility. The Al and Fe must eventually be precipitated; FeF_3, AlF_3, phosphate compounds or more complex mineral species will likely constitute a significant portion of pond sediments. Volatilization of either HF or of SiF_4 are the potential sources of any airborne emissions from the pond surface.

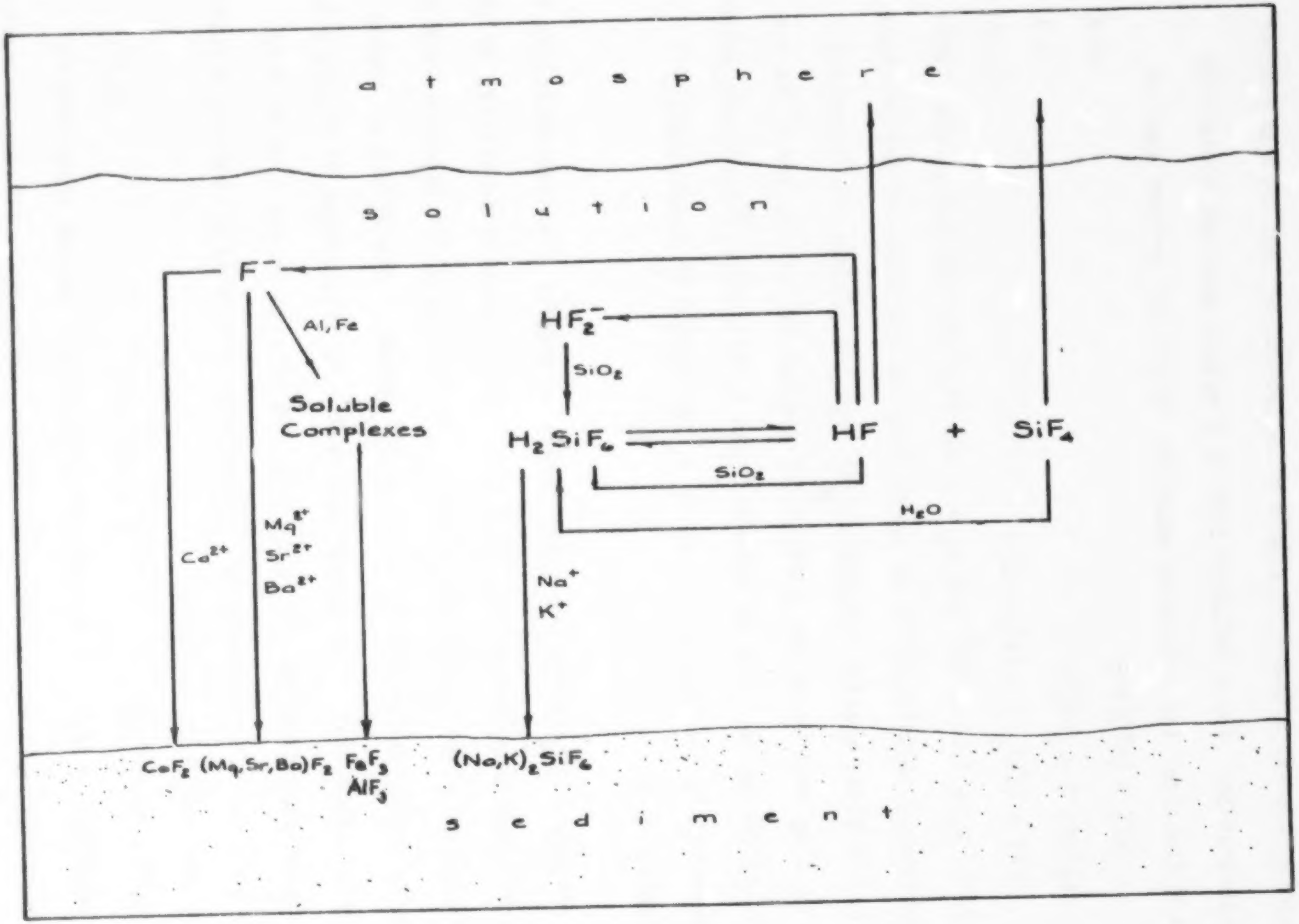


Figure 3.3 - Graphic Initial Description of some pertinent Gypsum Pond Reactions.

Farrer and Rossotti (1964) suggest that HF, HF_2^- and F^- are the only fluoride species present in simple HF solutions of less than one molar concentration. For a solution such as a gypsum pond was containing 0.4 M fluoride, the following equations relate the various species:

$$K_1[HF] = [H^+][F^-] \tag{3.8}$$

$$K_2[HF_2^-] = [HF][F^-] \tag{3.9}$$

$$[HF] + 2[HF_2^-] + [F^-] = 0.4 \tag{3.10}$$

At 24°C, $K_1 = 1.30 \times 10^{-3}$ and $K_2 = 0.102$ (Buslaeu and Gustyakove, 1965). Simultaneous solution of these three fluoride equations in the pH range of 1 to 8 gives species concentrations that are plotted in Figure 2.4. It can be seen that HF is the predominant species for pH <2, and F^- is predominant for pH >4. For pH between 2 and 4, all three species are present in appreciable quantities. At pH ≈2.8, the system is approximately equimolar in HF, HF_2^-, and F^-.

The rationale for liming the gypsum ponds to control fluoride emissions is apparent upon examination of Figure 3.4. An increase in pH results in the dissociation of HF, making the fluoride ion available for reaction with and reducing the concentration of volatile HF cations. The effect of liming on the HF concentration in gypsum pond water is illustrated in Figure 3.5. The dissociated fluoride can react with the calcium in the lime to form CAF_2, a relatively insoluble salt, which will precipitate removing a portion of the fluoride from solution:

$$Ca^{++} + 2F^- \rightleftarrows CaF_2, \qquad K = 2.5 \times 10^{10}. \tag{3.11}$$

This equilibrium can be a key one in controlling fluoride concentration in gypsum ponds without liming since gypsum, $CaSO_4 \cdot 2H_2O$, is near saturation in the pond waters providing excess calcium ions. In a similar manner,

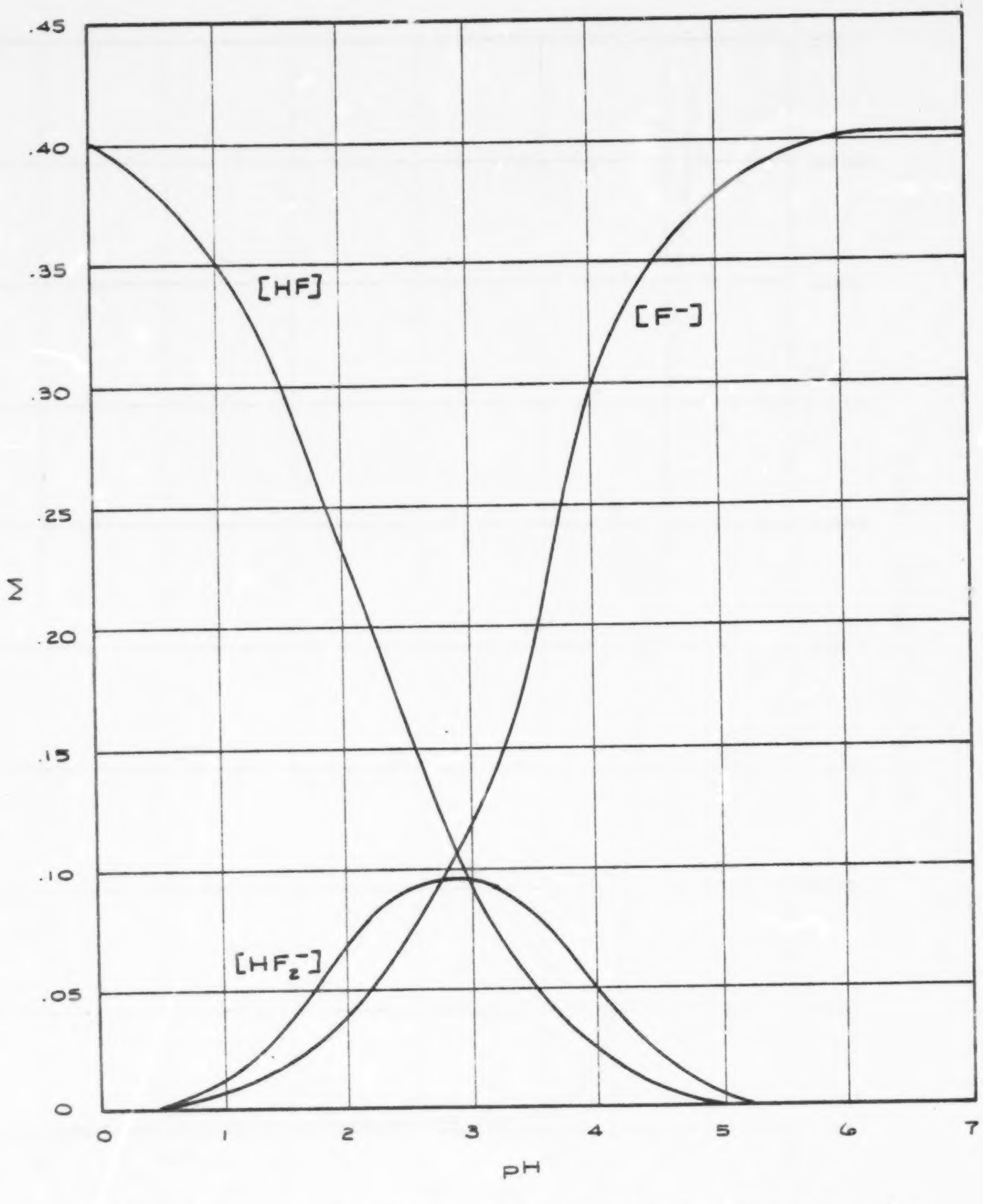


Figure 3.4 - Species Predominance Diagram for 0.4 M HF Solution.

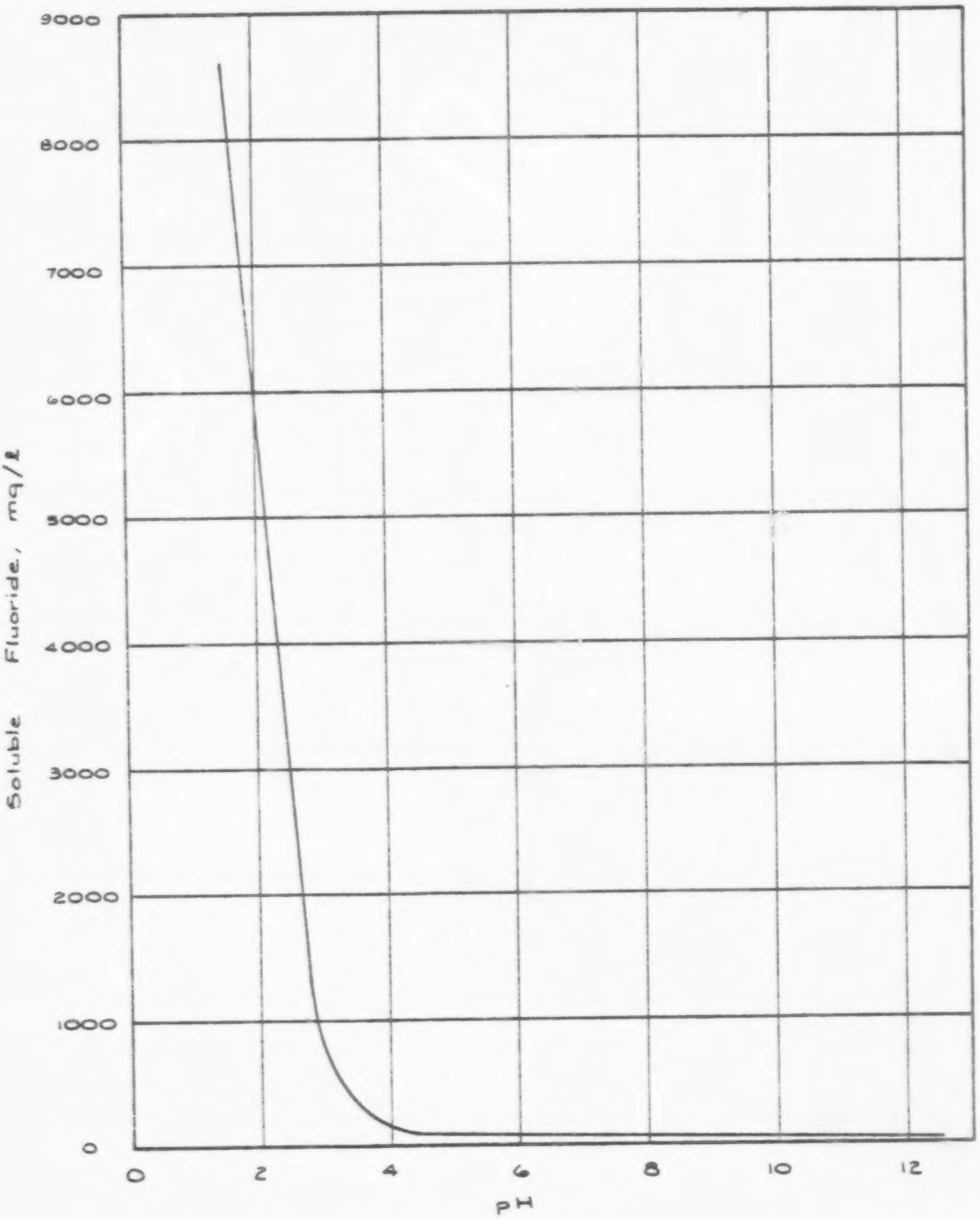


Figure 3.5 - Effect of Liming on Fluoride Evolution from Gypsum-Pond Water. (HEW, 1970)

F^- also forms insoluble precipitates with Mg, Sr and Ba which may be impurities in the phosphate rock.

Al and Fe readily complex fluoride in solution as indicated by the magnitude of the formation constants reported in Table 3.2. For a gypsum pond containing 0.019 $\underline{M}$ Al^{3+} and 0.005 $\underline{M}$ Fe^{3+}, the formation of the trifluoro species would consume 0.069 $\underline{M}$ F^-. The $[F^-]/[HF]$ ratio, while small, is sufficiently large to allow the complexation to proceed. Loss of HF from the solution through formation of soluble complexes is not accompanied by a compensating shift in the HF/H_2SiF_6 equilibrium as a result of inhibition by reaction of SiO_2 with any additional HF. The net effect of this complexation is to reduce HF concentration. This is 16 percent of the total $F^{\ominus}$ in the pond. It is reasonable to assume AlF_3 and FeF_3 will ultimately be incorporated into the pond sediment in low pH waters either in the hydrated form or as a more complex mineral association with gypsum. Al and Fe are continuously released from the phosphate rock matrix and there are no known volatile Al or Fe species, hence the sediment is the only possible final disposition.

All of the chemical reactions discussed above tend to remove F^- from solution and eventually incorporate fluoride into the sediment. This net transport of fluoride to the sediment affects all solution equilibria.

There exists one additional major pathway for transport of fluoride to the pond sediment. Fluosilicic acid will react with Na^+ and K^+ released from the phosphate rock matrix to form sodium and potassium fluorosilicates which are of relatively low solubility (7.62 and 1.77 g/l at

Table 3.2 Formation constants of Al and Fe fluoride species.

Complex Formation Reaction	Formation Constant
$Al^{3+} + F^- \rightleftharpoons AlF^{++}$	$K_1 = 1.4 \times 10^6$
$AlF^{++} + F^- \rightleftharpoons AlF_2^+$	$K_2 = 1.1 \times 10^5$
$AlF_2^+ + F^- \rightleftharpoons AlF_3$	$K_3 = 7.1 \times 10^3$
$Al^{3+} + 3F^- \rightleftharpoons AlF_3$	$K = K_1K_2K_3 = 1.1 \times 10^{15}$
$AlF_3 + F^- \rightleftharpoons AlF_4^-$	$K_4 = 570$
$AlF_4 + F^- \rightleftharpoons AlF_5^-$	$K_5 = 42$
$AlF_5 + F^- \rightleftharpoons AlF_6^=$	$K_6 = 3.0$
$F^3 + 3F^- \rightleftharpoons FeF_3$	$K = 1.2 \times 10^{12}$

25°C, respectively) and hence precipitate into the pond sediments as shown in Figure 3.3.

The chemical equilibria remaining to be discussed involve the complicated interactions of HF, HF_2^-, H_2SiF_6, SiF_4 and SiO_2. These reactions are as follows:

$$H_2SiF_6(aq) \rightleftharpoons 2HF(aq) + SiF_4(aq) \tag{3.12}$$

$$3SiF_4(aq) + 2H_2O \rightleftharpoons 2H_2SiF_6(aq) + SiO_2(s) \tag{3.13}$$

$$SiO_2(s) + 6HF(aq) \rightleftharpoons H_2SiF_6(aq) + 2H_2O(\ell) \tag{3.14}$$

$$HF(aq) + F^- \rightleftharpoons HF_2^- \tag{3.15}$$

$$3HF^- + SiO_2(s) + 3H^+ \rightleftharpoons H_2SiF_6(aq) + 2H_2O(\ell) \tag{3.16}$$

$$HF(aq) \rightleftharpoons H^+ + F^- \tag{3.17}$$

$$HF(aq) \rightleftharpoons HF(v) \tag{3.18}$$

$$SiF_4(aq) \rightleftharpoons SiF_4(v) \tag{3.19}$$

It is necessary to qualitatively consider the relative importance of these various reactions. They cannot be considered quantitatively at this point due to the overwhelming complexity of the interactions and the lack of basic chemical and empirical data related to the physical conditions encountered. As a first consideration, there will exist little SiF_4 in solution at any time due to the strong thermodynamic stability of the reaction products in (3.13) above (Simons, 1954). This fact essentially eliminates the potential for volatilization of SiF_4, as shown in reaction (3.19) from the surface of gypsum ponds.

Prior studies concerning gypsum pond chemistry have been based on the assumption that the dominant and hence controlling equilibrium is (3.12).

King (1971) summarized Tatera's (1970) ionization constant data and extended Tatera's curve to his gypsum pond water data. At 21°C,

$$K = \frac{[HF]^2[SiF_4]}{[H_2SIF_6]} = 3 \times 10^{-3}. \qquad (3.20)$$

Applying this expression directly to a pond water containing 0.42 moles/liter total $F^{\ominus}$ with the simplifying assumption that no other equilibria are involved, an equilibrium fluorine distribution of 50 percent of the fluorine as H_2SiF_6, 25 percent as HF, and 25 percent as SiF_4 is calculated.

This calculation, however, ignores all the other reactions listed above. SiO_2 plays a critical role in reducing the amount of HF in solution below the simplistically calculated proportion. Reaction (3.14) has an equilibrium constant of 2×10^{26} (Kirkland Othmer, 1964), indicating a strong balance toward the H_2SiF_6 rather than HF. Reaction (3.16) with SiO_2 also opposes free HF in solution. The predominance diagram, Figure 3.4, suggests the importance of the reaction of HF_2^- with SiO_2, since a considerable amount of HF_2^- appears to be available at gypsum pond pH levels. Judge (1971) concluded, in addition, that the reaction rate of SiO_2 with FH_2^- is approximately four to five times as fast as the reaction with HF.

Taking into consideration all of the above qualitative discussion of the relative significance of the various reaction pathways illustrated in Figure 3.3, a new figure (Figure 3.6) may be employed to illustrate only those reaction pathways considered to be most significant in a gypsum pond. This simplified model meets the criteria that all chemical species entering the gypsum pond must either precipitate into the pond sediments or volatilize and that waters in the pond are near saturation with respect to many chemical species due to continuous recycling.

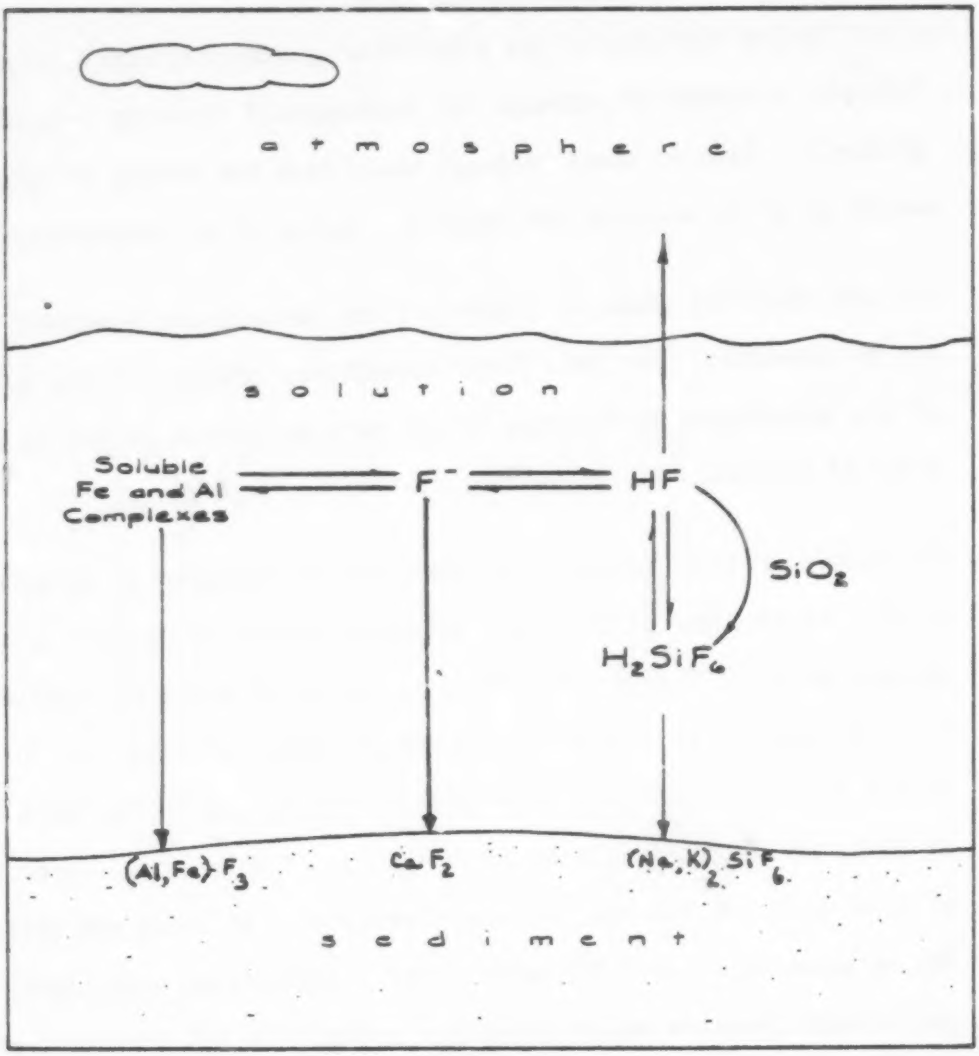


Figure 3.6 Major gypsum pond equilibrium

3.4 DISCUSSION OF THE SIMPLIFIED GYPSUM POND MODEL

A qualitative overview of the simplified gypsum pond model, Figure 3.7, indicates a number of pathways for transport of fluorine into the pond sediments. Each of these pathways would have the effect of reducing the amount of HF in solution and hence the amount of HF volatilized.

All the reactions shown in Figure 3.7 are temperature dependent and some are pH dependent. For this first assumption, however, it may be assumed pH and temperature in the pond do not vary to such an extent to affect the order of magnitude of the various equilibria involved.

The single critical pathway that must now be discussed is volatilization of HF. As an order of magnitude estimate, assume 25 percent of the $F^{\ominus}$ concentration of 0.42 M, the concentration of HF would be a maximum of 0.105 M. This corresponds to an equilibrium concentration of 2 mg/l HF in solution or a 0.02 percent solution of HF. Referring to HEW (1970) Table D-4, at 20°C, a 10 percent aqueous concentration of HF yields a vapor pressure of 0.14 mm Hg, so the maximum vapor pressure of HF above the gypsum pond may be expected to be 0.003 mm Hg under closed-system conditions. This small vapor pressure would indicate a low rate of net transport of HF into the atmosphere.

Additional thermodynamic analysis by Drs. Coots and Getzen (see O'Melia *et al*., 1975) suggests that HF (aq) may in fact be considerably lower due to the CaF_2 equilibrium. The value they suggest for the vapor pressure of HF above the Gypsum pond is 0.00008 mm Hg. This is probably a minimum since the possibility of formation of various calcium complexes was not considered.

3.5 SECTION 3 CONCLUSIONS

The development of the model of fluoride interactions presented in Figure 3.7 is based on little quantitative information. Available literature is deficient in the quantitative information necessary to evaluate this complex chemical solution. The model is based on several very qualitative assumptions concerning the significance of particular chemical reactions. Some reasonably detailed analytical data would be required to substantiate the conclusions drawn. Nevertheless, there appears to be little to support the contention that significant quantities of fluoride are emitted to the atmosphere by volatilization from the gypsum pond surface. This results from two conclusions: a) relatively little free HF and even less SiF_4, the only measurably volatile fluoride species, are present in the gypsum pond waters, and b) $HF_{(aq)}$ is of low volatility.

At least one of the assumptions used in arriving at this conclusion is supported by evidence available to the authors. Laboratory analysis of fluoride species in gypsum pond waters has indicated in excess of 80 percent is in the form of fluosilicic acid, H_2SiF_6. One other empirical observation bearing on the qualitative conclusions reached is that recycled gypsum pond water is used in the scrubbers which are designed to remove HF which is volatilized during several process steps. If these recycled waters have an HF concentration such that a significant quantity would be likely to volatilize in the pond environment, it is highly unlikely that these same waters would be effective in absorbing airborne HF in the scrubbers.

Researchers who have measured airborne fluorine concentrations in the vicinity of gypsum ponds have made no apparent attempt to differentiate between the particulate and non-particulate forms. It is possible that a large proportion of the fluorine detected near ponds results from fugitive dust from gypsum piles and gypsum deposits surrounding the pond and not as emissions from the pond surface.

4.0 DETERMINATION OF FLUORIDE EMISSION FACTOR

To date, three studies have been conducted in an attempt to determine the amounts of fluoride released to the atmosphere from gypsum settling ponds. The first study by Frank L. Cross, Jr. was performed in 1967. It consisted of measuring fluoride concentrations emitted from a small A-frame structure placed on a 160 acre gypsum pond. The second study conducted by B. S. Tatera in 1970 determined emission rates by placing water from a gypsum pond in an experimental wind tunnel. The third and final study determined fluoride emission rates by first determining a mass transfer coefficient for water, based on many experimental measurements from a large midwestern lake, and then relating the mass transfer coefficient of fluorides to that of water through existing mass transfer correlation. This study, by W. R. King, was conducted in 1973.

Each of the above studies was critically examined for scientific validity and consistency. In the following, each of these studies will be reviewed in the order presented above.

4.1 REVIEW OF CROSS AND ROSS' STUDY

The first known attempt to measure emissions from a gypsum pond was that of Frank L. Cross, Jr. of the Manatee County Health Department, Bradenton, Florida in 1967. This study was performed as a result of public concern over the potential fluoride emissions from a nearby fertilizer plant. Since results of fluoride emissions tests had indicated that the major plant stacks were well within allowable fluoride

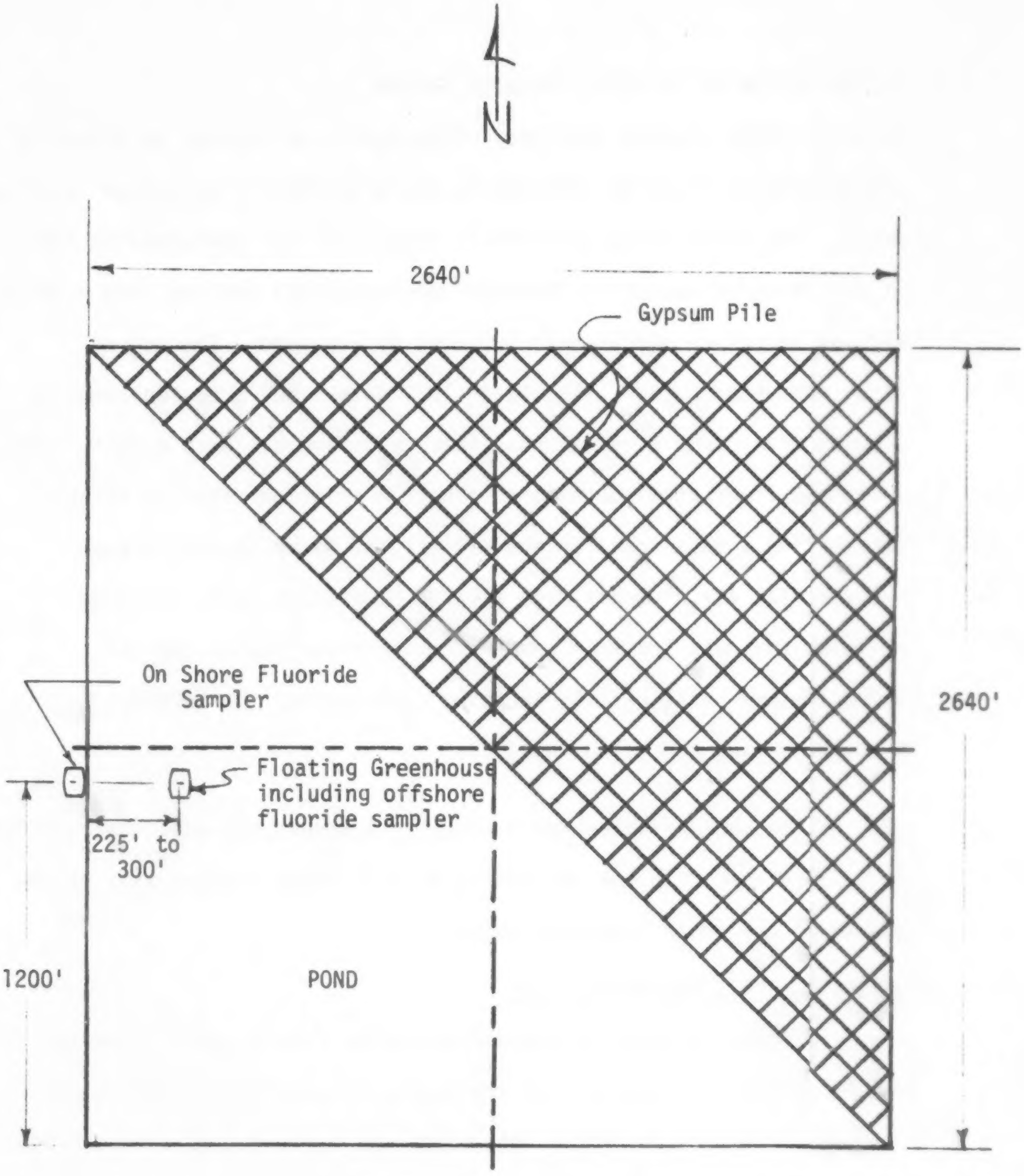
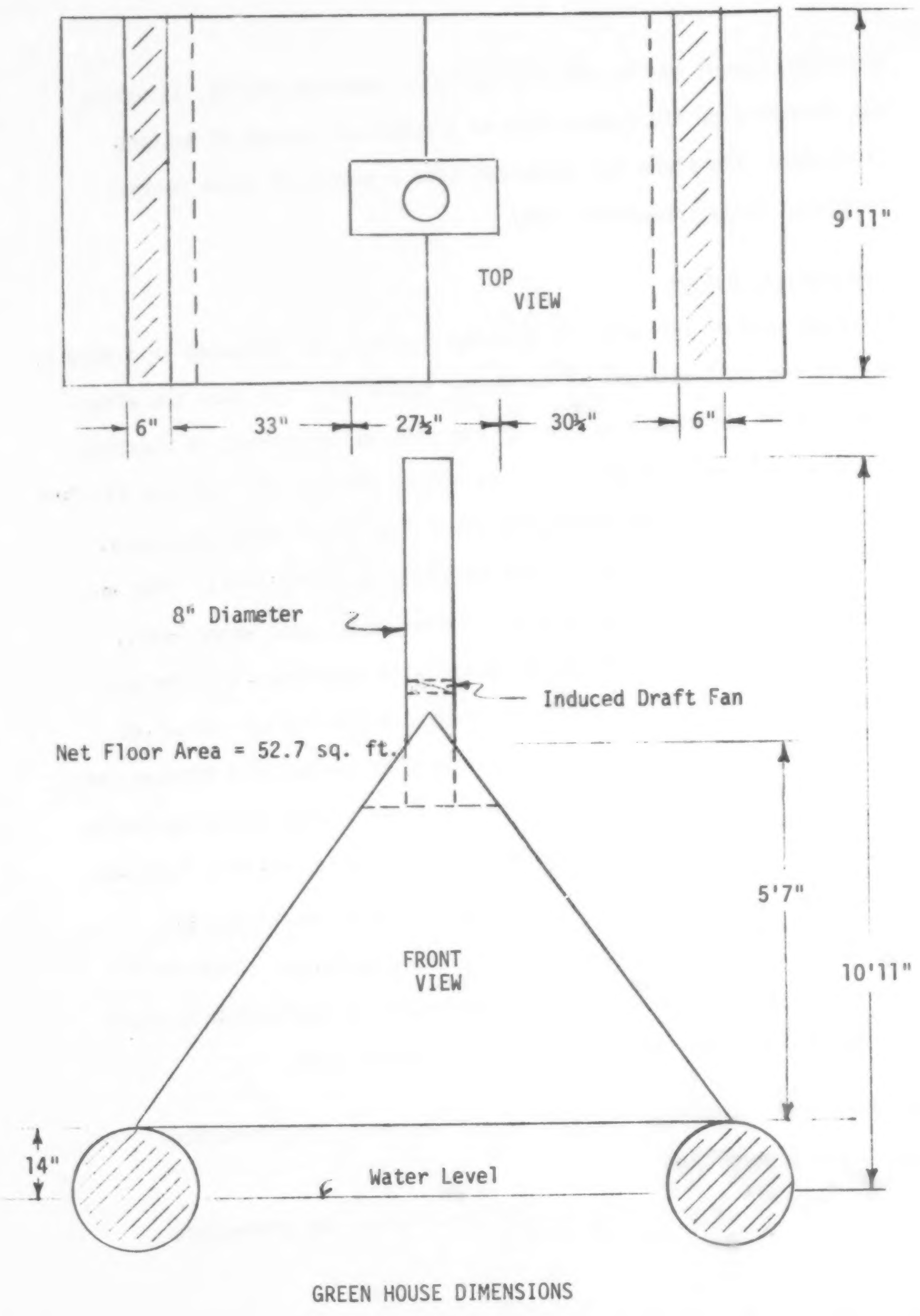

N
2640'
Gypsum Pile
2640'
On Shore Fluoride Sampler
Floating Greenhouse including offshore fluoride sampler
225' to 300'
1200'
POND

Figure 4.1. Location of A-Frame on Gypsum Pond.



GREEN HOUSE DIMENSIONS

GYPSUM POND TESTS

Figure 4.2. Dimensions of A-Frame Used by Cross.

emissions levels set by the Florida State Board of Health, attention was focused upon the gypsum pond as a potential source of ambient fluorides. The study was conducted over a period of three months, September through November, 1967.

4.1.1 Experimental Design

A gypsum pond of 160 acres in size was chosen. As indicated in Figure 4.1 half of the area was used as an active gypsum pile, so that the effective area of the liquid portion of the pond was 80 acres. A floating greenhouse, shown in Figure 4.2, was placed between 225 feet and 300 feet east of the shore. The greenhouse was a floating A-frame structure, covered by transparent plastic and supported by six barrels. The barrels kept the sides approximately 14 inches above pond water level, thus allowing for air interchange between the greenhouse and the environment. An 8-inch stack with an induced draft fan was installed on the roof, providing a constant flow rate of ambient air through the greenhouse. Ambient, 24-hour air samplers and a temperature recording device were placed within the greenhouse. A similar ambient fluoride sampler was located on the bank to provide comparison of ambient fluoride levels with those monitored in the greenhouse. Cross felt it was a requirement that the two measurements be approximately equal. The reasons, however, are unclear and unsubstantiated.

The following parameters measured were fixed constants throughout the experiment:

Q = Volumetric flow rate of air through the greenhouse stack = 225,500 ft^3/day

A_g = Projected area of greenhouse over the pond water = 52.71 ft^2

D = Diameter of stack = 8 inches

V_s = Velocity of air through the stack = 450 ft/min

A_p = Effective area of gypsum pond = 80 acres

The following independent variables were measured throughout the experiment:

T_p = Temperature of gypsum pond

T_g = Temperature of greenhouse

T_a = Ambient temperature above pond

V = Wind speed

W = Wind direction

Dependent experimental variables were:

C_g = Concentration of fluorides in greenhouse air $\left(\frac{\mu g F^-}{ft^3}\right)$

C_{os} = Concentration of fluorides measured at on-shore sampler

E = Fluoride emission rate (lb/acre-day) =

$$\frac{C_g \times Q}{A_g} \times \left(\frac{10^{-6}\ lb}{454\ \mu g}\right) \times \left(\frac{43,560\ ft^2}{acre}\right)$$

4.1.2 Experimental Results

The data in Table 4.1 were generated from six different days of observations. As seen, the maximum value given is 0.161 lb/acre-day. Cross, however, states that this is a minimum emission rate, for unknown reasons. Values as low as 0.04 lb/acre-day were obtained and the mean was 0.089 lb/acre-day.

4.1.3 Interpretation of Results

The first point to make concerning Cross' study is that no attempt was made to determine the parameters which influence gypsum pond emissions. No parameters were varied throughout the experiment which entered the emission calculation, except for the fluoride concentration measured within the greenhouse. However, the intention of his experiment was not to conduct an elaborate study, but to practically measure an emission rate of that pond during normal operating conditions.

Cross interprets the results to mean that all of the fluorides sampled in the greenhouse were evolved from the projected area A_g. Actually, the air entering the greenhouse contained fluorides which were transported into it as it moved across the pond before reaching the greenhouse. During the testing period, the wind blew predominantly from the northeast.

As shown in Figure 4.1, air from the northeast would have traversed approximately the same distance over the water on reaching the greenhouse sampler as on reaching the on-shore sampler. Thus one would expect the fluoride concentration in the greenhouse to be the same as that measured on shore provided the air flow through the greenhouse was at the proper rate.

Table 4.1. Results of Cross and Ross' Greenhouse Experiment on a Gypsum Pond.

Date	$C_g \frac{\mu g F^-}{ft^3}$	C_g ppb F^-	C_{os} ppb F^-	Q ft^3/day	A_g ft/day	E $\frac{lb}{acre\text{-}day}$
10/19/67	0.1374	6.3	6.3	225,500	52.7	0.057
10/20/67	0.1841	8.4	11.7	225,500	52.7	0.076
10/25/67	0.2240	10.2	15.6	225,500	52.7	0.092
10/26/67	0.3898	17.8	11.3	225,500	52.7	0.161
10/31/67	0.2653	12.1	10.9	225,500	52.7	0.109
11/ 1/67	0.0968	4.4	7.5	225,500	52.7	0.040

Cross assigned an arbitrary area (A_g) and an arbitrary flow rate (Q) to his system and to determine an emission rate multiplied the flow rate by the fluoride concentration and divided by the projected area. Had the area been twice as great, Q and C_g would have been approximately the same as before and an emission rate equal to half of that obtained before would have been measured. Similarly, had Q been doubled, A_g and C_g would have remained unchanged and an emission factor twice as great would have been obtained.

The conclusion is that fundamental errors caused by using an arbitrary area and flow rate render the results meaningless. No judgments can be made regarding accuracy of results since the method used is totally invalid.

4.2 REVIEW OF TATERA'S STUDY

One of the major studies conducted to date was that of B. S. Tatera. The purpose of his study was to determine which parameters affected gypsum pond emissions. His investigations were submitted to the University of Florida Department of Environmental Engineering as a Ph.D. dissertation in 1970.

Tatera's study consisted of two phases. In the first phase, he measured saturation vapor pressures of fluorides over liquid solutions of hydrofluoric acid (HF) or fluosilicic acid (H_2SiF_6) and distilled water or gypsum pond water. In the second phase, Tatera conducted a laboratory evaluation of the parameters that influence fluoride emissions from gypsum ponds. These were determined to be fluoride ion concentration, temperature and air velocity over the water surface.

4.2.1 Tatera's Vapor Pressure Studies

Tatera used a gas-saturation method for measuring fluoride vapor pressures, which consisted of a bubbler (or series of bubblers) containing the liquid solution. An inert gas was bubbled through the solution and the gas stream saturated in fluorides according to the vapor pressure of fluoride in equilibrium with a solution of a given concentration and temperature. Tatera measured the vapor pressure of fluorides in this fashion for the systems HF-H_2O, H_2SiF_6-H_2O, HF-gypsum pond water, and H_2SiF_6-gypsum pond water. Concentrations were varied over the range 0.1M - 0.5M (2,000 to 10,000 ppm F^-). Liquid temperatures for which data were gathered were 70, 85, and 100°F. In every case it was found that a linear relationship existed between fluoride concentrations and fluoride vapor pressures above the solution. Expressions derived for the system HF-H_2O were:

$$C_{af} = 614.7\ C_{sf} \qquad \text{at } 70°\text{F} \qquad (4.1)$$

$$C_{af} = 817.0\ C_{sf} \qquad \text{at } 85°\text{F} \qquad (4.2)$$

$$C_{af} = 1{,}032.9\ C_{sf} \qquad \text{at } 100°\text{F} \qquad (4.3)$$

For the system H_2SiF_6-H_2O, the equations derived were:

$$C_{af} = 48.0\ C_{sf} \qquad \text{at } 70°\text{F} \qquad (4.4)$$

$$C_{af} = 55.9\ C_{sf} \qquad \text{at } 85°\text{F} \qquad (4.5)$$

$$C_{af} = 80.3\ C_{sf} \qquad \text{at } 100°\text{F} \qquad (4.6)$$

For the system H_2SiF_6-pond water, the equations derived were:

$$C_{af} = 70.6\ C_{sf} \qquad \text{at } 70°\text{F} \qquad (4.7)$$

$$C_{af} = 80.7\ C_{sf} \qquad \text{at } 85°\text{F} \qquad (4.8)$$

$$C_{af} = 143.0\ C_{sf} \qquad \text{at } 100°\text{F} \qquad (4.9)$$

For the system HF-pond water, the equations derived were:

$$C_{af} = 106.5 + 523.6\ C_{sf} \quad \text{at } 70°\text{F} \qquad (4.10)$$

$$C_{af} - 183.7 + 892.8\ C_{sf} \quad \text{at } 85°\text{F} \qquad (4.11)$$

$$C_{af} = 223.6 + 1{,}177.8\ C_{sf} \quad \text{at } 100°\text{F} \qquad (4.12)$$

where:

C_{af} = concentration of fluorides in air $\left(\frac{\mu g}{ft^3}\right)$

C_{sf} = molar concentration of fluorides in solution

The above correlations show that for similar fluoride concentrations in a solution, fluorides in the form of H_2SiF_6 exert a lower vapor pressure than fluorides present as HF, by about a factor of 10. The above correlations were not used in the determination of an emission factor, but they do clearly show the dependency of fluoride vapor pressures upon fluoride concentration in the water.

4.2.2 Tatera's Wind Tunnel Study

The second phase of Tatera's study was concerned with the determination of a fluoride emission factor. His method involved the utilization of a tank as shown in Figure 4.3, containing gypsum pond water over which fresh air was passed as shown in Figure 4.4. The gypsum pond was constructed from black iron plate which formed a box, 2 feet wide, 6 feet long and 1 foot high. It was placed within a gypsum pond water bath 4 feet wide, 8 feet long and 14 inches deep. Temperature control was maintained by utilizing heating elements placed in the water bath. Water was recirculated between the pond and bath at the rate of 68 gallons per hour.

SCALE: 3/4" = 1'

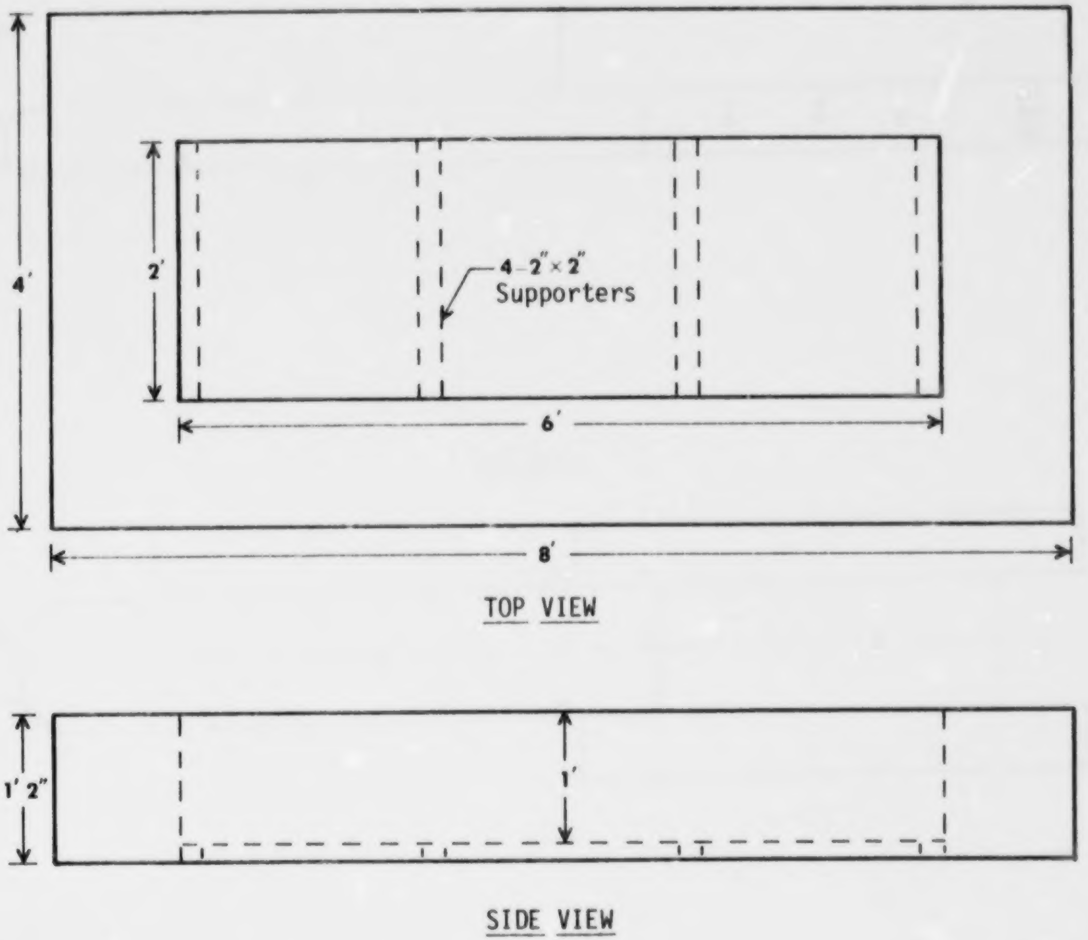


Figure 4.3. Model Gypsum Pond and Water Bath Used in Tatera's Gypsum Pond Studies.

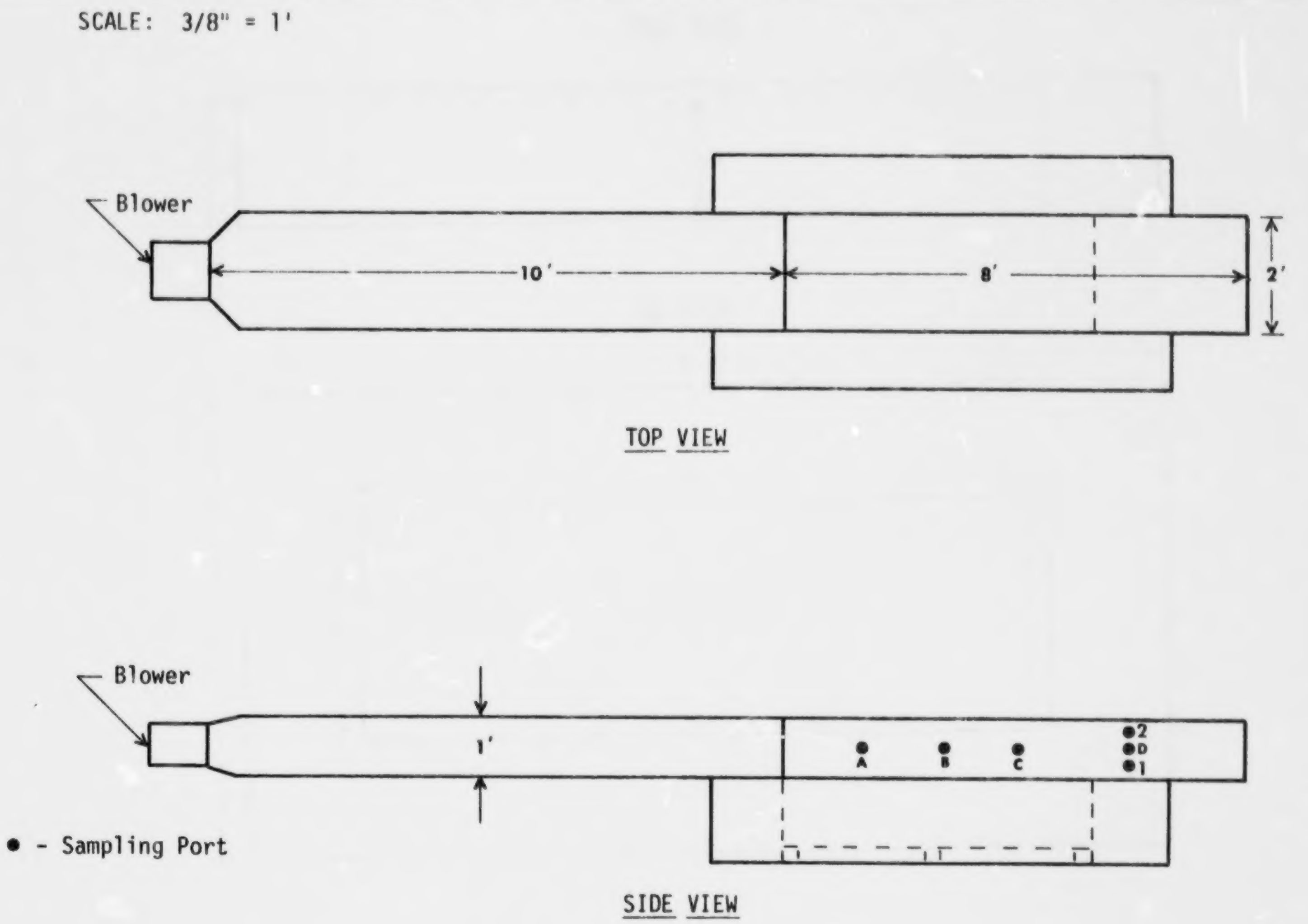


Figure 4.4. Schematic Diagram of Experimental Setup Used in Tatera's Gypsum Pond Studies.

A wind tunnel, 18 feet long, 2 feet wide, and 1 foot high ran from a 0.4 HP blower to and over the gypsum pond. Flow rate was controlled by means of baffles placed within the ductwork. Instruments were placed within the ductwork to accurately measure the average velocity through the ductwork. Sampling ports were installed at the locations shown in Figure 4.4. Fluoride concentrations at the end of the pond were measured by utilizing a stainless steel sampling probe connected to a series of impingers, filled with a fluoride absorbing solution of sodium acetate. The air was then pulled through a wet test meter by a vacuum pump.

Fluoride concentrations in the sampler were measured using an Orion specific ion electrode for fluorides with a calomel reference electrode and a Corning Model #10 pH and millivolt meter. Fluoride concentrations were determined according to:

$$C_a = \frac{C_s V_s M_f}{V_a} \qquad 4.13$$

where: C_a = concentration of fluorides in air sample $\left(\frac{\mu g}{ft^3}\right)$

C_s = molar concentration of fluorides in sample $\left(\frac{moles}{L}\right)$

V_s = volume of sample (L)

M_f = molecular weight of fluoride $\left(\frac{\mu g}{mole}\right)$

V_a = measured volume sampled at desired temperature (ft^3)

Experiments were conducted in duplicate at four different velocities or flow rates and at three different temperatures. An emission factor at each of the twelve conditions was determined in accordance with:

$$E = \frac{C_a \times Q}{A} \times \frac{43{,}560\ ft^2}{acre} \times \frac{lb}{4.54 \times 10^8\ \mu g} \times \frac{1{,}440\ min}{day} \qquad (4.14)$$

where: E = fluoride emission rate (lb/acre-day)

Q = air flow rate (ft^3/min)

A = area of pond = 12 ft^2

Results of the studies on process water are summarized in Figure 4.5. The resulting linear correlations, through the origin, are, at the 95 percent confidence level:

$$E = (0.00816 \pm 0.0015)\ V \quad \text{at } 75°F \qquad (4.15)$$

$$E = (0.0103 \pm 0.0042)\ V \quad \text{at } 85°F \qquad (4.16)$$

$$E = (0.0306 \pm 0.0061)\ V \quad \text{at } 95°F \qquad (4.17)$$

Where V = velocity measured at 0.1M height (ft/min)

4.2.3 Interpretation of Results

Tatera designed his experiment with some knowledge of the parameters that affect emissions, i.e., wind velocity, temperature and concentration. He developed vapor pressure data at various different liquid fluoride concentrations (equations 4.1-4.12), which indicated higher vapor pressures of fluorides when fluoride concentrations were increased in the liquid phase. Generally these were linear relationships, in accordance with Henry's Law:

$$P_f = HX_f \qquad (4.18)$$

where: P_f = partial pressure of fluoride in vapor phase (mm Hg)

H = Henry's constant of proportionality (mm Hg^{-1})

X_f = molar fraction of fluorides in liquid phase

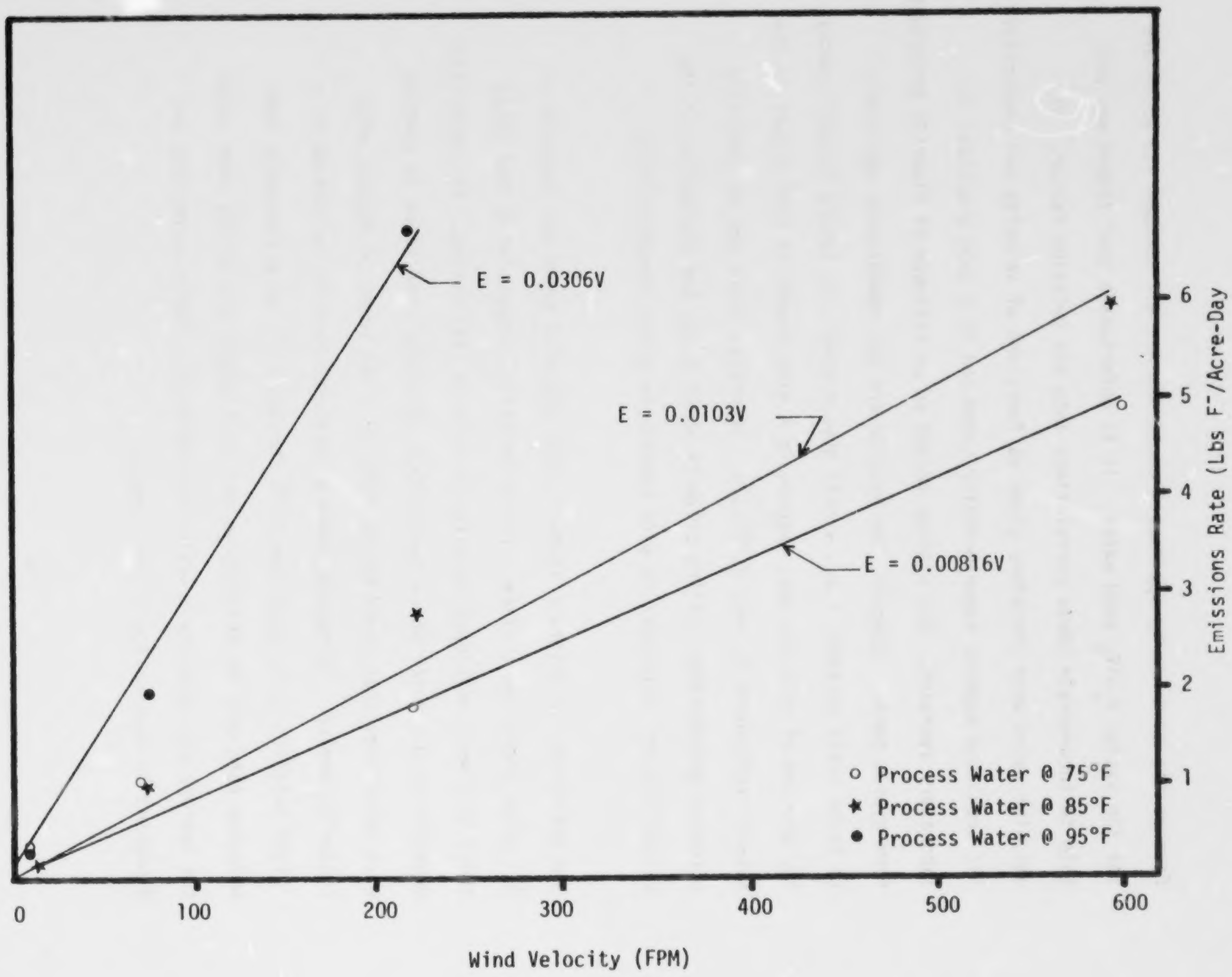


Figure 4.5 Tatera's Emission Factors for Process Water at 75°, 85°, 95°F.

Perhaps the most nearly applicable equations are 4.7 through 4.9 which are for the system H_2SiF_6 pond water. It is unfortunate that Tatera was not able to incorporate these correlations into his emission factor. His emission rates were therefore given as functions of velocity and temperature. His technique appears experimentally sound and is a good practical in-laboratory approach. His studies served as an estimate of fluoride emissions from gypsum ponds. However, the results are not immediately applicable to large scale systems, i.e., a real gypsum pond. As Tatera himself states, the problem of relating what happens in a wind tunnel to what occurs in the natural atmosphere is very difficult. Secondly, there are no generally accepted hydrodynamic scaling criteria which allow the evaluation of the suitability of prototypes in wind tunnels to actual concentrations.

One deficiency in Tatera's study is that the wind speed was measured at 0.1 meter above the surface. It can be readily appreciated that since there is a well developed velocity profile in real systems, the velocities measured at 0.1 meter above the surface should be readjusted to conform with velocities that would be recorded by a met tower or ambient wind measuring device. Therefore, when an emission rate is calculated at a given velocity using equations 4.15 through 4.17, an erroneously high emission rate will be obtained unless wind speeds are scaled down using the appropriate velocity profile relationships. These correcions are discussed in section 4.4 of this report.

4.3 REVIEW OF KING'S STUDY

W. R. King conducted a study under U.S. Environmental Protection Agency Grant No. R-800950 for the determination of fluoride emissions from gypsum ponds. This probably represents the most complete study of the problem to date.

4.3.1 Method Of Approach

The general approach used in King's study was to determine a mass transfer rate for volatile fluorides into an air stream passing over gypsum pond water. King, in accordance with common practice, defined his emission rate according to the expression:

$$N_f = K_f \left(P_f^* - P_f\right) \tag{4.19}$$

where

N_f = Fluoride transfer rate per unit surface area from pond to atmosphere $\left(\frac{\text{g-moles F}}{\text{hr-M}^2}\right)$

K_f = Overall gas-side fluoride mass transfer coefficient $\left(\frac{\text{g-moles F}}{\text{hr-M}^2 - \text{mm Hg}}\right)$

P_f^* = Partial pressure of fluoride at the gas liquid interface in equilibrium with pond water (mm Hg)

P_f = Partial pressure of fluorides in the atmosphere above pond.

The term $(P_f^* - P_f)$ is commonly known as the gradient or driving force for mass transfer from a region of high concentration to a region of low concentration, i.e. from the gas-liquid interface to the bulk air stream.

Unfortunately at the beginning of the study, there was no information available regarding K_f and unreliable information concerning P_f^* and P_f. Thus a determination of an emission factor necessitated that information be developed and experiments be conducted to determine the real values of the unknown quantities.

King's approach in the determination of an emission factor was:

1. Development of a correlation for predicting the mass transfer coefficient (K_f) from existing data.

2. Measurement of the equilibrium vapor pressure (P_f^*) of fluorides over samples of pond water.

3. Prediction of fluoride mass transfer rates by equation (4.19).

Since King arrived at an emission factor by conducting laboratory scale experiments in the determination of vapor pressures and by utilizing mass transfer coefficients developed for another species (water), the applicability of the emission factor to an actual gypsum pond required field verification. The procedure used by King to accomplish this task involved:

1. Development of a computer simulation through the use of a Gaussian dispersion model incorporating equation 4.19 to predict downwind fluoride concentrations.

2. Measurement of ambient fluoride levels downwind of a gypsum pond.

3. Comparison of measured and predicted downwind concentrations resulting in the verification of the computer simulation and it component parts, including the emission prediction method.

4.3.2 Development of Mass Transfer Coefficient

Since no experimental mass transfer coefficient data was available describing the evolution of fluorides from gypsum ponds, King utilized a theoretical correlation developed from studies using short flat plates and fitted the form of this correlation to data available on mass transfer of water from a large lake. By use of a diffusivity correction, results obtained for the water system were modified to yield a correlation describing the mass transfer of fluorides from a pond.

Some correlations for turbulent mass transfer systems have been developed by use of analogies with similar heat transfer systems. The main analogy relating heat and mass transport is that proposed by Chilton & Colburn.

$$J_D = J_H = 1/2\ f = \text{function of Reynolds Number} \tag{4.20}$$

where

$$J_H = \frac{Nu}{Re\ Pr^{1/3}}$$

$$Nu = \frac{h\ X}{K} = \text{Dimension less heat transfer Nusselt Number}$$

$$Re = \frac{XV\rho}{\mu} = \text{Dimension less Reynolds Number}$$

$Pr = \frac{C_p \mu}{k}$ = Dimension less Prandtl Number

h = Heat transfer coefficient

k = Thermal conductivity

μ = Viscosity

X = Characteristic length

v = Velocity

C_p = Heat capacity at constant pressure

ρ = density of bulk stream

$J_D = \frac{Nu_{AB}}{Re\ S_c^{1/3}}$

$NU_{AB} = \frac{Kx\ X}{c\ D_{AB}}$ = Dimension less mass transport Nusselt Number

$Sc = \frac{\mu}{\rho D_{AB}}$ = Dimensionless Schmidt Number

Kx = Mass transfer coefficient

D_{AB} = Diffusivity of binary system A-B

c = Molar concentration of receiving stream

f = Dimensionless skin friction factor - function of Reynolds Number

It can be seen from the above that it is only necessary to determine exactly what the functional relationship of the friction factor, F, to the Reynolds number, Re, and to subsequently equate it to J_D. For turbulent flow over a flat plate, Schlichting obtained the following empirical expression for the average friction factor over an entire flat plate:

$$f = 0.072\ (Re)^{-1/5} \qquad (4.21)$$

This expression, however, was developed for, and directly applicable to, a small flat plate under conditions of turbulent flow and a 1/7 power velocity distribution.

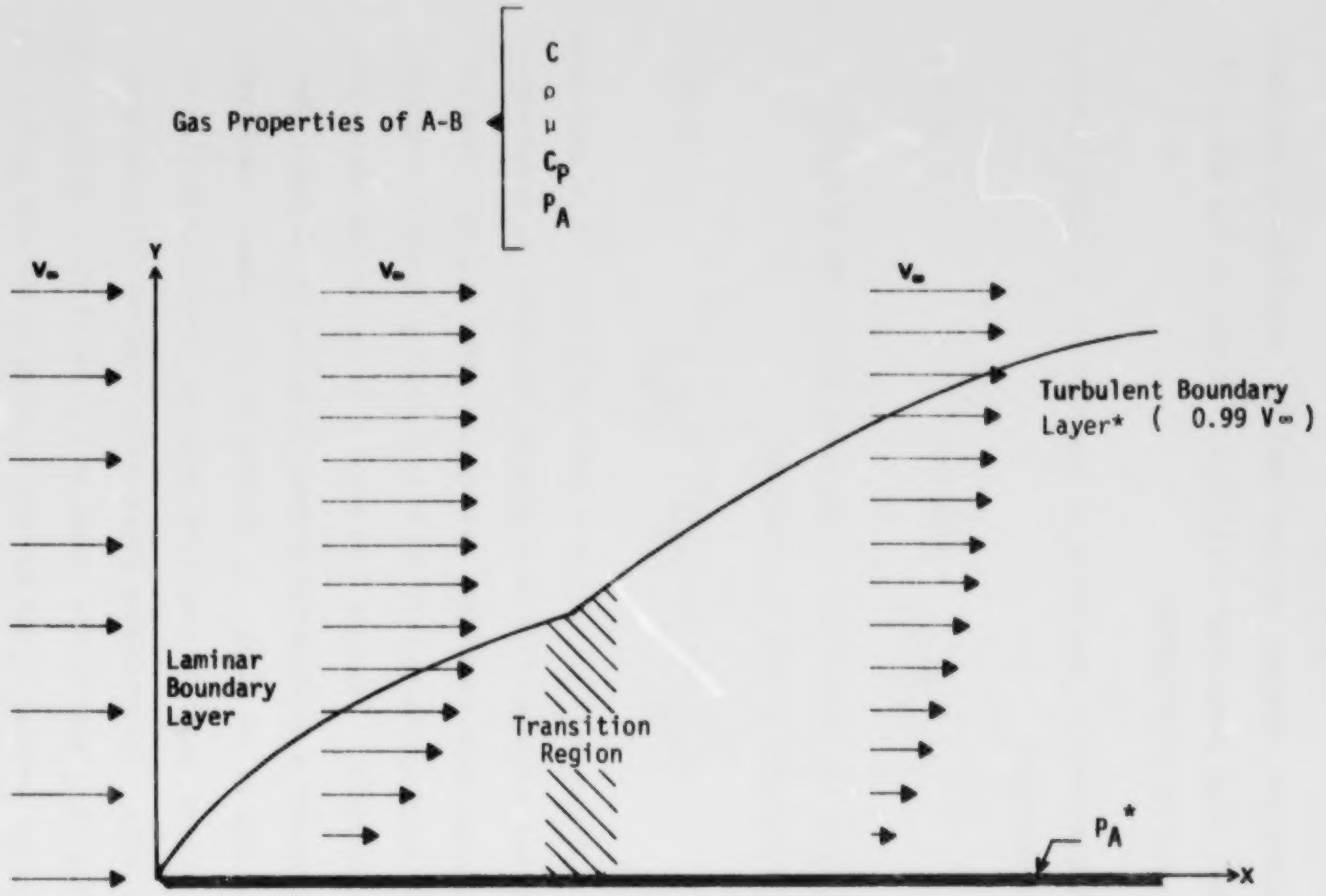
Upon substitution of equation 4.21 into 4.20 the following relationship is obtained:

$$\frac{Nu_{AB}}{Re\ Sc\ 1/3} = 0.072\ Re^{-1/5} \qquad (4.22)$$

According to the definitions of the terms above, the following relationship used by King is obtained:

$$\frac{\bar{K}x\ X}{c\ D_{AB}} = 0.036 \left(\frac{\rho V X}{\mu}\right)^{4/5} \left(\frac{\mu}{\rho D_{AB}}\right)^{1/3} \qquad (4.23)$$

Figure 4.6 indicates the system to which equation 4.23 is applicable. A thin semi-infinite plate of a volatile substance, A, evaporates under steady-state conditions into an unbounded gaseous stream of A and B which approaches the plate tangentially in the X direction with velocity V_∞. Species B is present in the gaseous phase only. At the instant a differential element of moving gas contacts the leading edge of the plate, the velocity of that element immediately drops to zero, which is consistent with the concept of no-slip at the boundary. Instantaneous deceleration requires infinite force, therefore, T_x, which is the stress on a plane of fluid moving in the X direction parallel to the surface is equal to infinity at $x = 0$, $y = 0$.



* Boundary layer below plate is omitted.

Figure 4.6. Tangential Flow Distribution Along a Sharp-Edge Semi-Infinite Flat Plate with Mass Transfer Into Stream.

As the fluid element moves along the surface, a laminar region builds up in which the flow is less than V_∞. Eventually, at a length Reynolds Number $\left(\frac{\rho V_\infty X}{\mu}\right)$, Re = 10^5, this layer becomes turbulent in nature and it is in this region that equation 4.23 applies.

At this point, a few comments regarding the use of equations 4.20-4.23 are in order.

1. Equation 4.20 as applied to mass transfer has been shown to be accurate in describing evaporation of water from a circular vessel at the bottom of a wind tunnel. However, these experiments were conducted in the laminar flow regime. Although the analogy between heat and mass transfer is quite good, some question remains about extending this experiment to a large body of water.

2. Equation 4.21 has been verified for small flat plates and is based on a 1/7 power velocity distribution.

3. The assumption is made that the evaporating species is a pure component in the liquid phase. Applications involving dilute solutions involve the possibility of large liquid mass-transfer resistances.

4. The flat plate can operate at steady-state, in that at any position, X, there is no change in any property with

time, but it can never operate in fully developed flow because the boundary layer continues to increase regardless of how long the plate is.

In applying equations 4.20-4.23 to a gypsum pond, the following points should be considered:

1. Equation 4.20 has not been shown to hold for mass transfer from large bodies of water such as a gypsum pond. It is basically useful in heat and mass transfer equipment design, but not necessarily in a large system.

2. Equation 4.21 does not describe the relationship between friction factor and Reynolds number for a pond. An expression, specific to that situation, would have to be experimentally derived.

3. In a gypsum pond, King was interested in a dilute volatile component, i.e., fluorides. The flat plate assumes a pure component. A pond would be nearly pure water, but data developed from it would not be easily transferred to apply to fluorides by use of equations 4.20-4.23.

4. Air over the pond would be in fully developed turbulent flow due to contact with a land surface prior to passing over water.

In view of the above, the flat plate analysis is judged to be inapplicable to the situation of evaporation of water from a gypsum pond and less applicable in describing fluoride evolution from such ponds.

Equations 4.20-4.23, while not directly applicable to a gypsum pond, do, however, give insight into which variables affect mass transfer coefficients. It can be seen from equations 4.20-4.23 that:

$$K_x = f\ (X,\ c,\ D_{ab},\ V,\ \rho,\ \mu,\ C_p) \qquad (4.24)$$

Since certain variables would be constant for a given system, the effect of the other variables on K_x can be studied.

$$K_x = f\ (X,\ V) \text{ at constant } (c,\ D_{ab},\ \rho,\ \mu,\ C_p) \qquad (4.25)$$

Based on his use of equations 4.20-4.23, King assumed the relationship to be:

$$K_x = aX^{-0.2}\ V^{0.8} \qquad (4.26)$$

Verifying equation 4.26 or determining the correct functional relationship in equation 4.25 will not yield information regarding the relationship of K_x to C, D_{ab}, ρ, μ, or C_p. Any inferences regarding the relationship between K_x and D_{ab} from equations 4.20-4.23 need experimental verification.

4.3.2.1 Mass Transfer for Coefficient From Evaporation Studies

King's analysis of the fluoride emission problem began by assuming equations 4.23 and 4.26. His next step was to develop a mass transfer coefficient for water evaporating in air, with the thought that in doing so, he could infer information pertinent to the fluoride problem.

An extensive amount of data had been collected for evaporation rates of water from lakes and reservoirs. The study King chose to evaluate was conducted by the U.S. Geological Survey at Lake Hefner, Oklahoma.

In this study, the U.S.G.S. compared different mass transfer equations with measured evaporation rates. In analyzing the Lake Hefner study, King used only those data that the U.S.G.S. personnel estimated had potential errors in evaporation rates of less than 0.03 in/day (Class A data). Of these 142 daily observations, King further eliminated 29 data points in which the humidity driving force was less than 1 mm Hg, the evaporation rate was less than 0.02 in/day or where the signs of the humidity driving force and evaporation rate did not agree. He analyzed the remaining 113 data points and derived an expression relating the average mass transfer coefficient of water to the velocity of air above the water.

$$\overline{K} = 0.432\ V_{16}^{0.82} \tag{4.27}$$

where

$$\overline{K} = \frac{\text{gm - moles } H_2O}{\text{hr - } M^2 \text{ mm Hg}}$$

V_{16} = wind velocity measured at 16 meters above the lake surface

Equation 4.27 indicates the hypothesis that K is proportional to velocity raised to the 4/5 power is correct. No significant length effect was discerned. However, it should be noted that confirmation of the velocity relationship does not yield information regarding the relationship of mass transfer coefficients to all of the variables indicated in equation 4.24.

Upon incorporating similar data from various evaporation pans with the Lake Hefner data and setting the velocity exponent equal to 0.8, King obtained the following correlation which he considered the best estimator of the overall, gas-side mass transfer coefficient for the transfer of water from a pond or lake to the atmosphere.

$$K = 0.429\, V_{16}^{0.8} \qquad (4.28)$$

An analysis of variance was performed on the data which indicated that at a given wind speed, the observed mass transfer coefficient would lie between 0.67 and 1.50 of the value predicted by equation 4.28 with 95 percent confidence. Stated differently,

$$K_{observed} = K_{predicted} \pm \begin{matrix} 50\% \\ 33\% \end{matrix} \qquad (4.29)$$

at the 95 percent level of confidence, for water evaporating from a large body of water, such as Lake Hefner.

Harbeck (1962) analyzed evaporation data for Lakes Hefner and Mead and several other smaller bodies of water. In his analysis, Harbeck found that the mass transfer coefficient, N (at constant velocity), varied with the square root of the surface area.

$$N \propto (A^{0.5})^{-.10} \qquad (4.30)$$

The equation predicts that the mass transfer rate for a 100 acre pond would be 17 percent greater than for a 2,300 acre lake (Lake Hefner). In applying equation 4.28 to a pond, an appropriate correction factor incorporating equation 4.30 would be in order. However, this factor should be applied to each pond depending on its size and geometric configuration.

4.3.2.2 Derivation of Mass Transfer Coefficient

By writing equation 4.23 for the species water evaporating from a flat plate into a stream of air, we have:

$$\frac{\overline{K}_{aw}\ X}{c\ D_{aw}} = 0.036 \left(\frac{\rho V X}{\mu}\right)^{0.8} \left(\frac{\mu}{\rho\ D_{aw}}\right)^{1/3} \qquad (4.31)$$

A similar expression for fluorides is:

$$\frac{\overline{K}_{af}\ X}{c\ D_{af}} = 0.036 \left(\frac{\rho V X}{\mu}\right)^{0.8} \left(\frac{\mu}{\rho\ D_{af}}\right) \qquad (4.32)$$

where:

$\overline{K}_{aw}$ = average overall gas-side mass transfer coefficient for water evaporating into air $\frac{\text{g mole}}{\text{hr - M}^2\ \text{mmHg}}$

$\overline{K}_{af}$ = average overall gas-side mass transfer coefficient for fluorides evaporating into air $\frac{\text{g mole}}{\text{hr - M}^2\ \text{mmHg}}$

D_{aw} = binary diffusivity for a water vapor-air system $\frac{\text{cm}^2}{\text{sec}}$

D_{af} = binary diffusivity for a fluoride air system $\frac{\text{cm}^2}{\text{sec}}$

By dividing equation 4.31 by 4.32, King obtained the following expression:

$$\frac{\overline{K}_{aw}}{\overline{K}_{af}} = \left(\frac{D_{aw}}{D_{af}}\right)^{2/3} \qquad (4.33)$$

This expression is questionable, however, since the relationship of K to D was not verified for the system under consideration. One can utilize the expression above in predicitng a mass transfer coefficient for fluorides from a flat plate, consisting of pure or nearly pure fluorides. However, even in a flat plate the above equation might not work when the two species are evaporating simultaneously and one species is orders of magnitude more dilute than the other.

As a result of equation 4.33, King felt that it was only necessary to obtain diffusivity values for water and fluorides. The diffusivity of water was readily available and by using standard approximation methods, he calculated diffusivities for the assumed volatile species, HF and SiF_4.

It is important to know exactly which fluoride species is being evolved from the pond water. King seems to have gone astray in his reasoning at this point, for he proposes the following reaction occurring:

$$H_2SiF_{6(1)} \rightarrow 2HF_{(g)} + SiF_4\ (g) \qquad (4.34)$$

He then calculates an "effective fluoride" diffusivity from the following equation:

$$D_{af} = \frac{2\ D_{a\text{-}HF} + 4\ D_{a\text{-}SiF_4}}{3} \qquad (4.35)$$

It is difficult to understnad what rationale King had for formulating this diffusivity since equation 4.35 implies that somehow a mechanism is in effect which causes the molecules to diffuse more rapidly than either species would independently. Although King was trying to relate the diffusivity to molecular fluoride, this is not the correct approach for the above mentioned reasons and for those reasons that follow. According to Illarionov, the molar ratio of HF/SiF_4 in the vapor phase over a 1.09 weight percent solution of H_2SiF_6 (0.5 m) is about 12. Using this logic, it is proposed that an "effective diffusivity" based on a weighted average be derived as follows:

$$D_{af} = \frac{12\ D_{a\text{-}HF} + 4\ D_{a\text{-}SiF_4}}{16} \tag{4.36}$$

$$= \frac{12\ (0.234) + 4\ (0.106)}{16}\ \frac{cm^2}{sec} = 0.202\ \frac{cm^2}{sec}$$

This is a more appropriate value. First of all, it lies between 0.234 $\frac{cm^2}{sec}$ and 0.106 $\frac{cm^2}{sec}$ which is intuitively correct. Secondly, it incorporates the more accurate composition of volatile species. King estimated a value for effective fluoride diffusivity of 0.297 $\frac{cm^2}{sec}$. It is reasonable then, that equation 4.33 in King's report be changed from $K_{af} = 0.484\ V_{16}^{0.8}$ to $K_f = 0.374\ V_{16}^{0.8}$.

The conclusion drawn at this point regarding the mass transfer coefficient for fluorides is that it is probably correct within an order of magnitude. As a first approximation for a mass transfer from the liquid-gas interface into the bulk air stream, one could assume that it would be similar to that of water. King's value for K_f is 13 percent higher than K_{aw}. It is felt that King's value is a good order of magnitude approximation but that more information should be obtained concerning mass transfer coefficients for fluorides as related to water. This could possibly be determined through an approach similar to that used by Tatera. That is, a wind tunnel study using pond water could be conducted to confirm the relative transfer coefficients between fluorides and water.

4.3.3 King's Vapor Pressure Studies

Having obtained what he considered to be an accurate mass transfer coefficient, King proceeded to conduct equilibrium vapor pressure studies on gypsum pond water in order to develop an emission rate of the form indicated in equation 4.19 of this report.

King designed a system to conduct his vapor pressure studies that would:

1. Use actual, undiluted pond water with bottoms slurry present in order to maintain the various solid/liquid equilibria.

2. Provide information regarding the effect of temperature upon the fluoride vapor pressure over the solution.

3. Give information from two different ponds for the purposes of comparison.

By using an Othmar still, King was able to insure the establishment of a vapor-liquid equilibrium and maintenance of the liquid-solid phase equilibrium. His results are presented in Figure 4.7. While the technique is scientifically sound, two observations regarding the results can be made:

1. There is a pronounced minimum between 80 and 90°F.
2. The precision of the measurements is very poor.

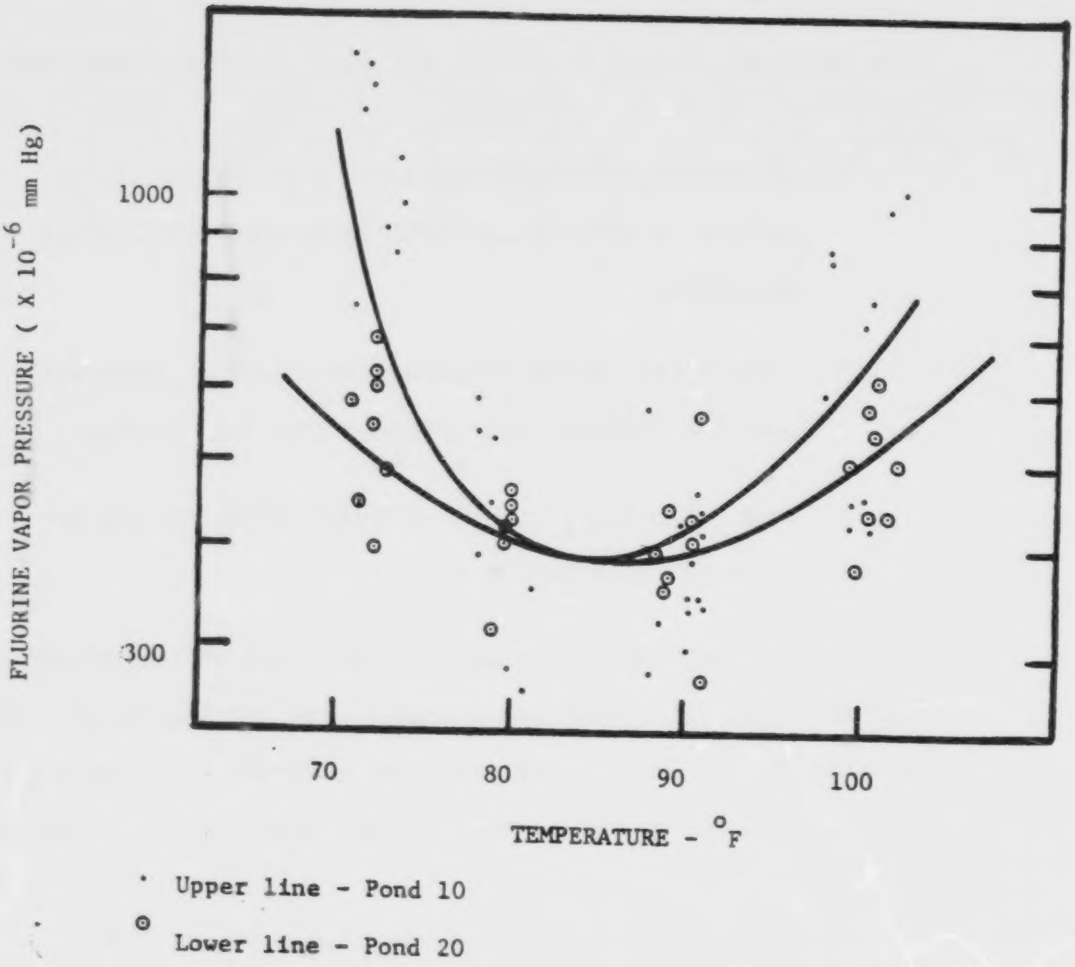


Figure 4.7. Fluorine Vapor Pressure Over Pond Water.
Source: King, 1970

3. A difference in vapor pressures exists between the two ponds.

With regard to the first point, one would expect a continual rise over the temperature range. It is very likely related to the transformations between the various fluoride species in solution (HF, HF_2^-, F^-, AlF_x, FeF_x, H_2SiF_6, SiF_4, etc.) as a result of the complex equilibria occurring between them.

The second point is demonstrated in Table 4.2, which shows a variance analysis for several of King's vapor pressure measurements. As this Table shows, the 95 percent confidence limits for two ponds at two different temperatures ranged from 33 to 60 percent. This is not totally unexpected, however, given the low concentration of fluoride being measured. It does reflect on the overall accuracy of the methods King uses in his verification of emission estimates.

Both King and Tatera state that vapor pressure is not a strong function of the fluoride level in pond water. However, at a temperature of 100°F, which is the most representative temperature of pond water, the average fluoride vapor pressure for pond 20 (0.335 g moles/l fluorides) was about half of the value obtained from pond 10 (0.628 - 0.800 g moles/l fluorides).

Table 4.2 Analysis of Variance for King's Vapor Pressure Data.

POND 10--0.628 gm moles F^-/L

Temperature	Data Points	mmHg x 10^{-6} (Mean)	Standard Deviation	95% C.L. (± 2σ)
90°F	9	327	67	41%
100°F	8	591	178	60%

POND 20--0.336 gm moles F/L

Temperature	Points	mmHg x 10^{-6} (Mean)	Standard Deviation	95% C.L. (± 2σ)
90°F	7	410	79	38%
100°F	9	477	78	33%

The vapor pressure studies fall short on the following points:

1. No comparison was made between pH and vapor pressure.
2. No rigorous study was made between fluoride vapor pressure and composition.

Due to the variability in chemical composition of gypsum ponds, the vapor pressure studies should not be applied to all ponds. It is immediately obvious that at 100°F emissions from pond 10 would be greater than the amount emanating from pond 20.

4.3.4 Fluoride Emission Factor

King gives no algorithms to describe his fluoride emission factor. The shape of the vapor pressure curves preclude this. He does present families (Figures 4.8 and 4.9 are reproduced from King's report) of curves from which an emission rate is calculated for pond 10 and pond 20. The families of curves describe the relationship indicated in equation 4.19 as a function of temperature and wind speed.

If there were no errors introduced in deriving a fluoride mass transfer coefficient from the water studies, the emission factor could, at best, be accurate within ± 90% with 95% confidence. This is based upon the scatter in mass transfer data as well as vapor pressure data, as stated previously. However, the method of calculating a fluoride mass transfer coefficient by use of data from the evaporation of water is an order of magnitude approximation. Therefore, it is concluded here that King's emission factors are also order of magnitude approximations and are not rigorously applicable to all gypsum ponds.

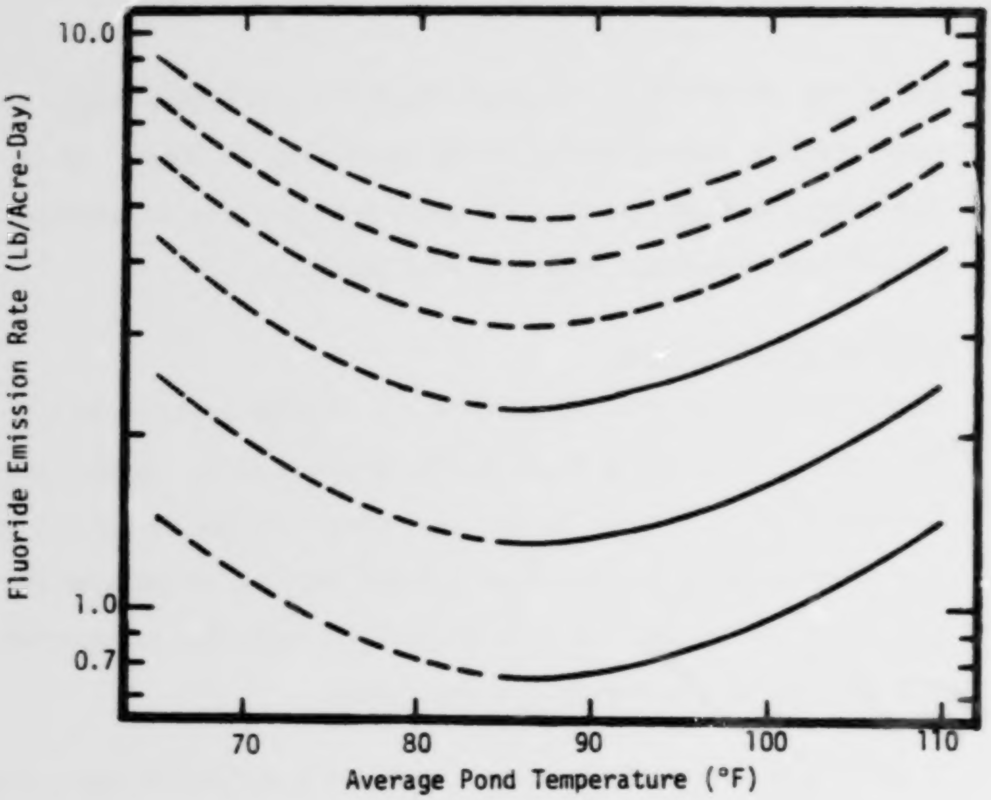


Figure 4.8. Fluoride Emission Rates for Ponds with Water Containing 0.336 g moles/liter Fluorides, V = Wind Speed at 16 Meters in Meters Per Second. (Source: King 1974).

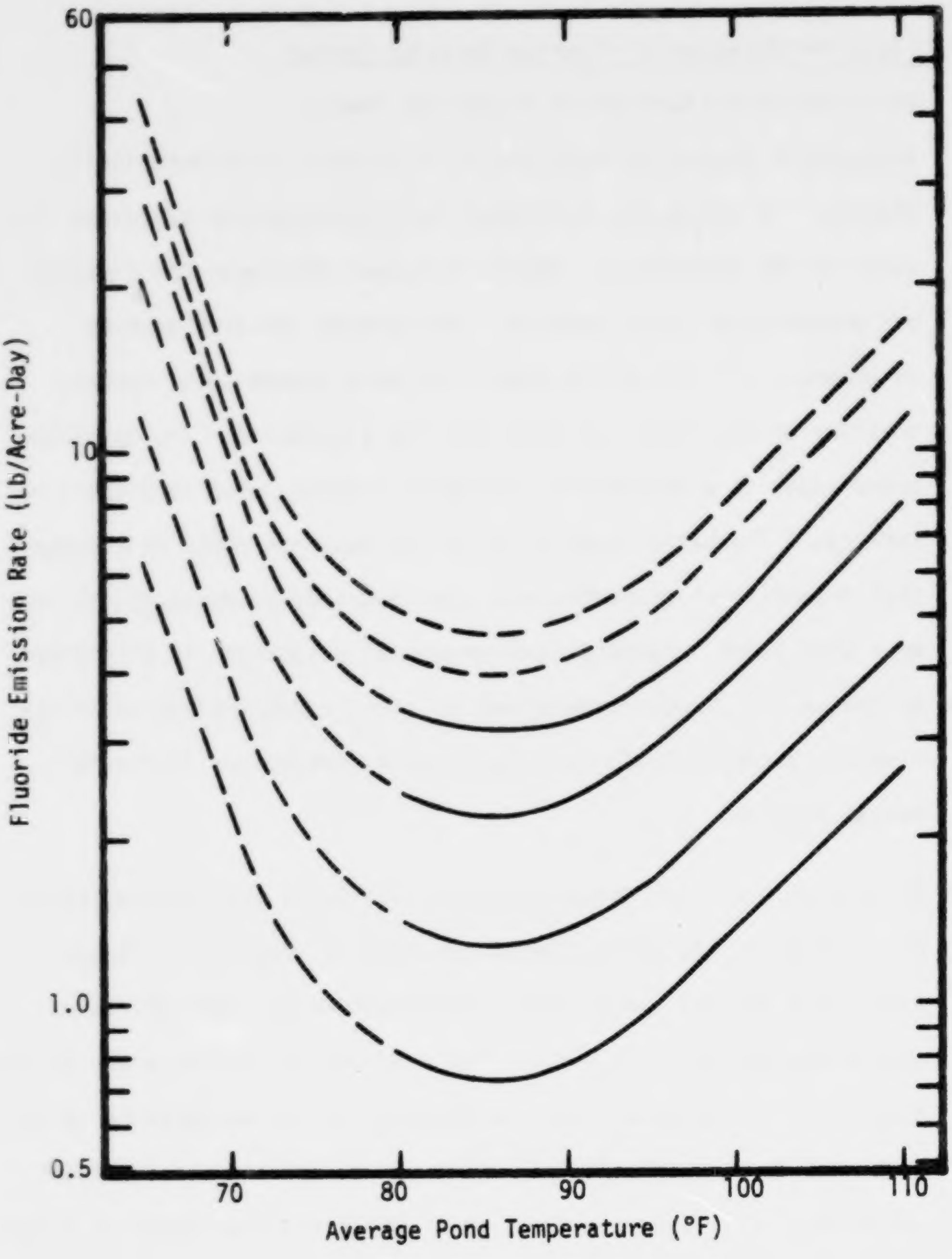


Figure 4.9. Fluoride Emission Rates for Ponds with Water Containing 0.628 g moles/liter Fluorides V_{16} = Wind Speed at 16 Meters in Meters Per Second.
(Source: King 1974).

4.3.5 Field Verification of Fluoride Emission Factor

4.3.5.1 Verification/Calibration of Dispersion Models

Atmospheric dispersion modeling is an attempt to mathematically simulate the transport, diffusion and transformation processes that occur in the atmosphere. Models have been developed for elevated and ground-level point sources, line sources and area sources. In general, all dispersion models estimate ground-level concentrations of substances emitted into the atmosphere. The Gaussian plume model is a theoretical treatment commonly used in dispersion modeling. The basic formulation of the Gaussian equation assumes that ground-level concentrations are inversely proportional to the mean wind speed. Vertical and horizontal dispersion is simulated by the use of standard deviations of plume concentration distribution for various stability categories, as determined from experimental studies.

To be confident that dispersion model estimates are representative of the real world, validation/calibration is necessary. Theoretical mathematical models have limitations which cause estimated concentrations to be in error. The availability and accuracy of the input data to the model and the accuracy of the mathematical algorithm are the significant influences on the accuracy of the model estimates. Similarly, calibration of the dispersion model is affected by the location, exposure and representativeness of the air sampling sites and by the accuracy of the air quality data. In validation or calibration, known pollutant emission rates, plume characteristics and meteorological data are combined to calculate ground-level concentrations for specific time periods and locations. The time periods and locations correspond to those for which ambient concentration measurements were obtained or are available. The calculated and measured concentrations are compared and a statistical relationship obtained (normally a linear regression analysis) If the statistical relationship is significant the model is calibrated and the relationship obtained is applied to all future concentration estimates by the model.

4.3.5.2 Prediction of Fluoride Concentrations Downwind of Gypsum Ponds

King developed a computer model whereby the simulation of dispersion of fluoride emissions from gypsum ponds was attempted. Area source emissions from the gypsum ponds were represented by a number of line source emissions. The explicit form of the Gaussian plume equation for a finite line source was utilized to describe dispersion of emissions from the line sources. The Gaussian finite line source equation is as follows:

$$x\ (X,\ 0,\ Z) = \frac{2q}{\sqrt{2\pi}\sigma_z\ U}\ \exp\left[-\frac{1}{2}\ \frac{Z}{\sigma_z}^{2}\right]\ x \int_{p1}^{p2} \frac{1}{\sqrt{2}\pi} \exp\ (-0.5\ p^2)\ dp \quad (4.37)$$

where:

x = concentration at (X, 0, Z)

X - downwind distance

Z = receptor height

q = line source emission rate per unit length

U = mean with wind speed

σ_y, σ_z = horizontal and vertical dispersion parameters

$P_1 = y_1/\sigma_y$

$P_2 = y_2/\sigma_y$

y_1, y_2 = limits of line source

The dispersion parameters, σ_y and σ_z, are functions of downwind distance as given by Turner (Turner, 1970).

Uncertainties enter into the Gaussian finite line source equation through several parameters. These parameters include source emission rate (q), the dispersion parameters (σ_y and σ_z) and the mean wind speed (U). Accurate measurement of the mean wind direction is also important in verification, since this establishes the source-receptor relationship used in the model for concentration calculations. Proper verification/calibration of the dispersion model requires an accurate knowledge of these parameters, and the usefulness of the model will depend upon the uncertainty associated with these parameters.

Uncertainties in specifying the fluoride emission rate from the pond contributes to errors in the model concentration estimates. Since pollutant emission rate (q) enters directly into equation 18, the magnitude of the imposed error in the model due to inaccuracies would be equal to the error in the emission rate equation. As described in Section 3.3.4, the emission rate equation is at best accurate only within ± 90% at the 95% confidence level.

Another source of uncertainty in the dispersion model is in the specification of the horizontal and vertical dispersion parameters, σ_y and σ_z. King's use of σ_y and σ_z is within the assumptions under which the parameters were experimentally determined, i.e., sampling time of about 10 minutes, height; the lowest several hundred meters of the atmosphere, and the surface relatively open country. Even so, for distances of travel up to a few hundred meters from the source for all stabilities, σ_z may be expected to be correct only within a factor of two (Turner, 1970).

King continuously recorded wind speed and direction with on-site meteorological instruments in his field work. Type or manufacturer of the instruments was not mentioned in King's work. Assuming that the measurement instruments were properly calibrated and that they meet Atomic Energy Commission guidelines for wind measuring devices, they can be expected to measure wind speed within 0.5 mph and wind direction within ± 5 degrees. With this degree of accuracy, the wind speed measurements would be known within ± 7 percent (at 7 mph wind speed). These uncertainties in the wind speed and direction specification in the dispersion model would add to the uncertainty in concentration estimates by the model, and would affect the comparison of those estimates with measured concentration values.

Errors are inherent in simulating an area source by a number of finite line sources (refer to Figure 4.10). The simulation error lies in the initial emission density or apportionment. Area source emissions are initially emitted into a large volume of air since the emissions are apportioned over an entire area. By dividing the area source into a number of segments and concentrating each segment's emissions into line source emissions in the simulation model, the emission density is altered.

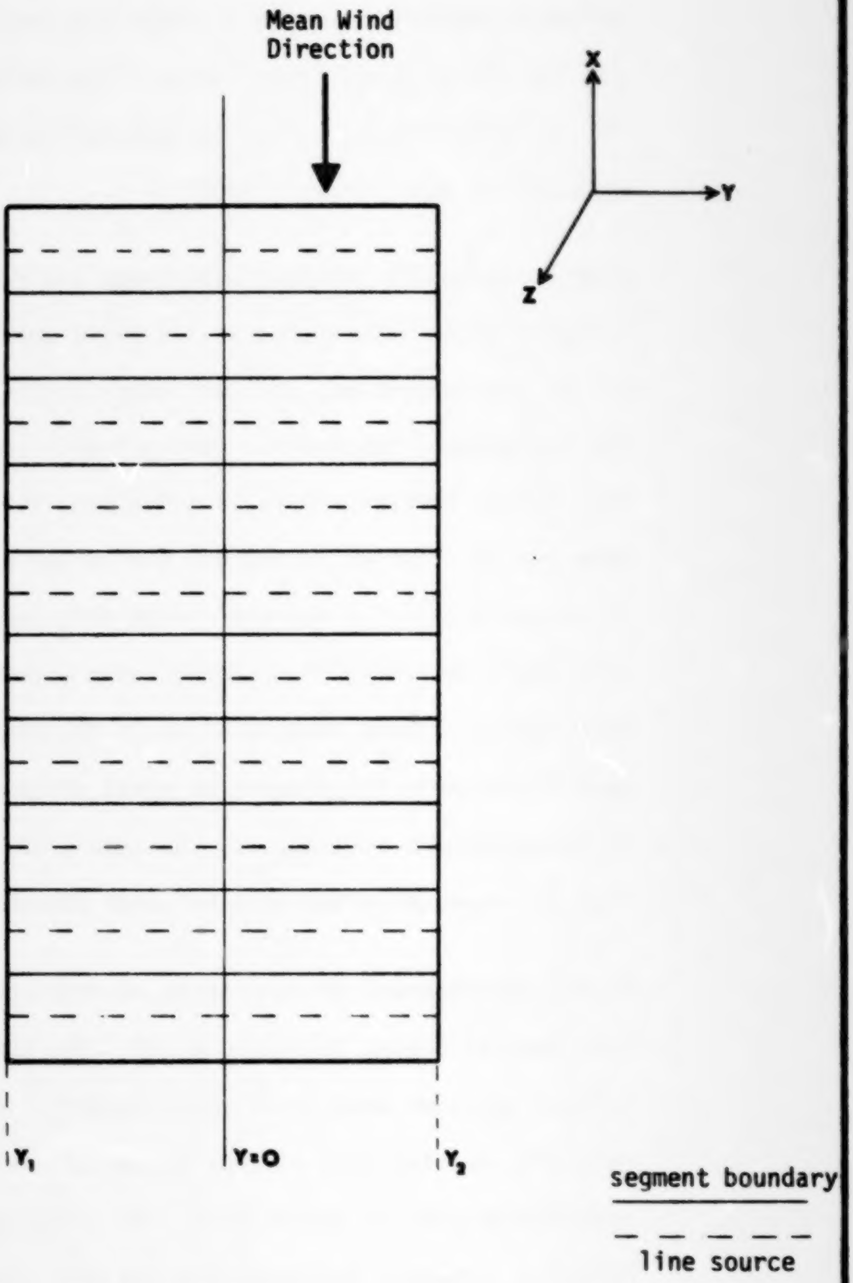


Figure 4.10. Line Source Simulation of a Rectangular Area Source.

The magnitude of error introduced due to this technique is dependent on the line source spacing used for the simulation, as well as the source-receptor distance (see Section 5.3). A smaller line source spacing will more closely simulate area source emissions, and therefore the model-simulated concentration pattern will closely resemble that expected from a real area source. Receptors close to the line-source simulated area source are affected to a greater extent than those further away. In practice, iterations are commonly made a part of the computer model in order to obtain an optimum spacing of line sources, or a sensitivity analysis is performed. King does not mention either of these procedures in his pond simulation model, wherein he used a 10 meter line-source spacing. The effect of varying the line-source spacing on concentration patterns is discussed in Section 5.3.

4.3.5.3 Ambient Fluoride Sampling Study

King used ambient samplers designed to measure HF concentrations in the vicinity of ponds 10 and 20. Each station consisted of a sampler with a capture element as shown in Figure 4.11, which was reproduced from King's report. Absorbing medium was a 2 g/l solution of Na_2CO_3 which flowed at a rate of 8-12 drops per minute along the inside diameter of the capture element. Ambient air, entering at an inlet 1.67 meters above the ground, was continually drawn through 30 feet of coiled tubing at a rate of 30 liters/minute. This allowed sufficient liquid gas contact to effectively absorb 95 percent of ambient

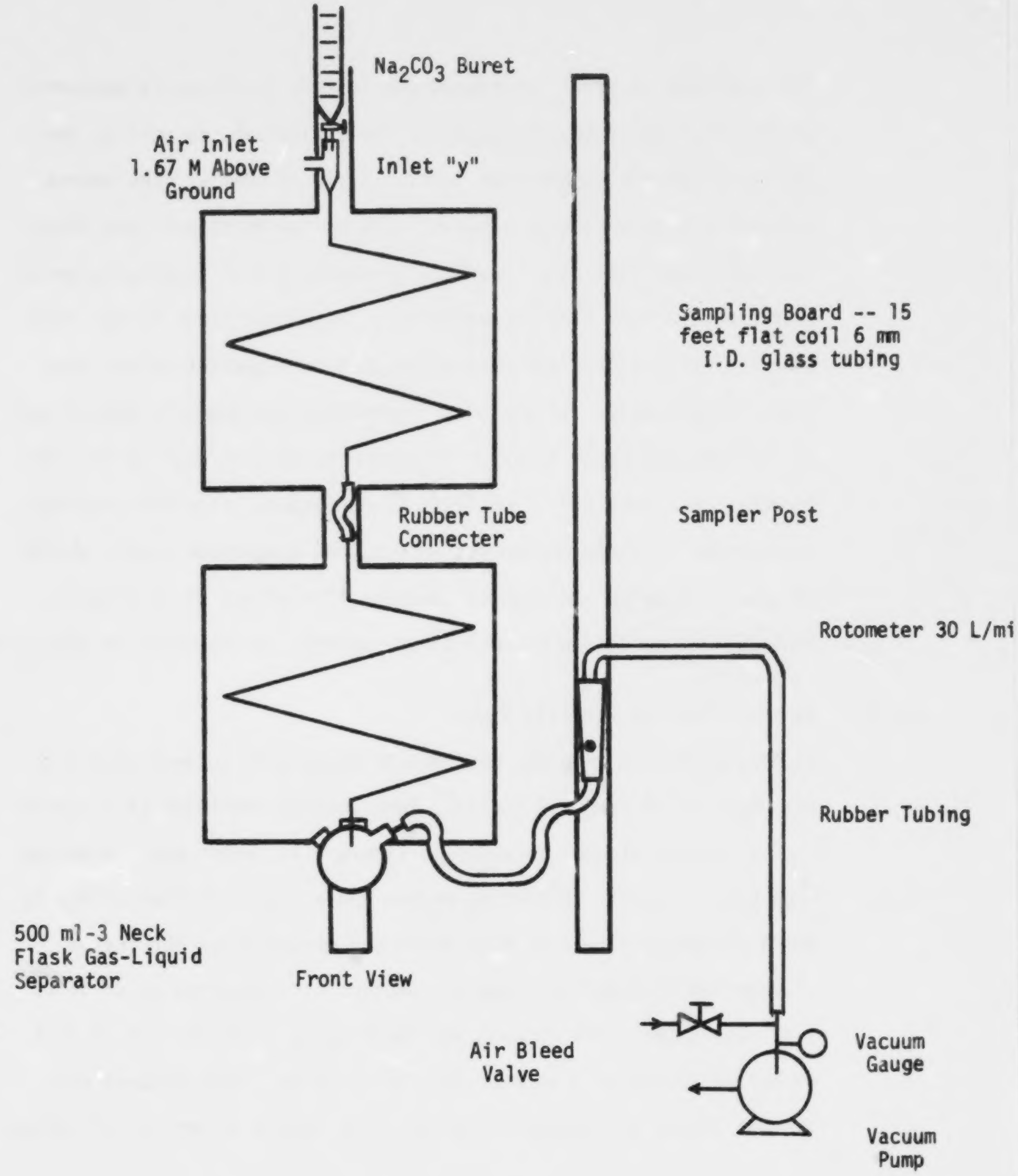


Figure 4.11. Ambient Air Sampler Used in King's Study.

air fluoride. The absorbing solution flowed into a liquid-gas separator from which the sample was taken for lab analysis. The air stream was pulled through a rotometer by a vacuum pump. The absorbing solution was analyzed in the laboratory for its fluoride content in order to determine ambient fluoride concentrations through the use of a fluoride spécific-ion electrode.

The use of the automatic "HF gas analyzer" is logical, since most likely it is HF that is evolved from gypsum ponds. However, particulate fluorides from the gypsum piles could cause positive interference by contributing to the fluoride level measured by the analyzer. This possibility can be readily appreciated since the disposal areas can be as high as 120 feet around the ponds. The original design of the fluoride sampler calls for a vertical absorption tube. This allows the absorption of HF and, in conditions of laminar flow, minimizes particulate-liquid contact. By using coiled tubing, a cyclonic effect is induced which causes particulate matter to be scrubbed out of the gas stream. This could be averted by the use of a teflon filter at the air inlet, but no indication that such a filter was used was evident in King's report.

The exact errors that particulate matter would contribute are not possible to assess since particulate fluoride emission rates from the piles would have to be known, as would any background concentrations in the area. King did not address this problem in his experimental design or analysis of results which precludes drawing any firm conclusions from his field work regarding gaseous fluoride emission.

4.3.5.4 Comparison of Measured and Predicted Fluoride Concentrations

Chapter 10 of King's work purports that significant correlations between the simulation model predicted fluoride concentrations and measured concentrations were obtained at the 95 percent confidence level for both pond 10 and pond 20. However, these correlations were obtained only after deletion of much of the data. Only 95 of 132 measurements were used in the analysis. Justification for deletion of these data in some cases does not seem to be valid, based on the information contained in the report. However, the author was not contacted to discuss the deletions.

In the analysis of pond 10, certain measured concentrations at Sampler 01 were not included in the analysis because the measured concentrations were much higher than predicted concentrations calculated by the simulation model. Figure 4.12 is a sketch of pond 10. These measured concentrations occurred when the average wind speed was between 5 and 6.3 m/sec. Justification was based on the contention that the dispersion model could not accurately predict concentrations when high wind speeds and short downwind distances existed.

A wind speed of 5 to 6.3 m/sec is well within the assumptions of the Gaussian plume model and the conditions under which σ_y and σ_z were derived (Turner, 1970). The model used by King should therefore be as accurate at wind speeds of 5 to 6.3 m/sec as it is at wind speeds of 1 to 5 m/sec. The data should not be rejected then on the basis of model errors at wind speeds of from 5 to 6.3 m/sec.

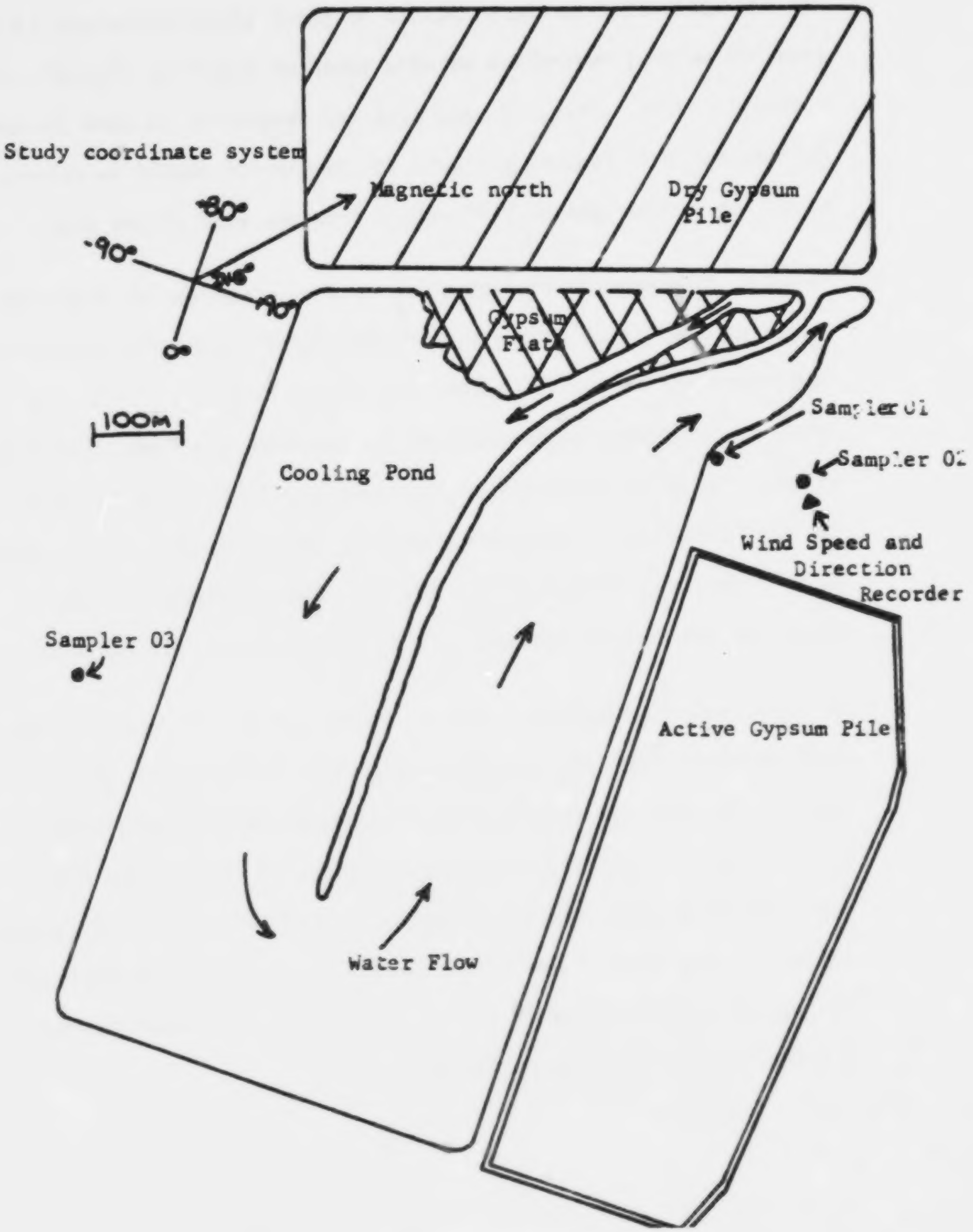


Figure 4.12. Pond 10 Layout (After King).

The dispersion parameters σ_y and σ_z used in the Gaussian plume model are not applicable to the situation of short travel distances (less than 100 meters) regardless of wind speed or stability (Turner, 1970; Pasquill, 1974). Thus, if some data for Sampler 01 at pond 10 were deleted for this reason, all data for Sampler 01 should be deleted since the sampler was only 10 meters from the edge of the pond.

Finally, the measured concentration data rejected due to high wind speeds at Sampler 01 show a significant correlation with calculated concentrations at the 99 percent confidence level ($r = 0.90$, d.f. = 6). However, calculated concentrations are consistently lower than measured values. In spite of King's conclusions, the model seems to work well for this situation, although corrections should be made in the model so that measured concentrations are not underestimated. A logical place for this correction would be in the emission rate equation.

Several measured fluoride values collected at pond 10 were deleted from analysis under the hypothesis that the active gypsum pile northeast of the pond was contributing significant quantities of ambient fluoride at the sampling locations (Samplers 01 and 02; see Figure 4.12). The simulation model predicted concentrations well below the measured values in most cases. The active gypsum pile could foreseeably contribute to high fluoride values at the samplers from both gaseous and particulate fluoride evolution.

A study of the plot sketch of pond 10 and of the wind directions presented in the Appendix of King's work for the usable measured concentrations at pond 10 indicate that the mean wind direction must be towards the stated direction in order for the gypsum pond to contribute to fluoride levels at the samplers. The majority of these usable measurements fell within the directions of -15 to 76 degrees (based on the pond 10 coordinate system). The measurements not used for pond 10 analysis were obtained with a mean wind direction of from 55 to 93 degrees, with only one measurement greater than 90 degree wind direction. The pond 10 sketch indicates that these mean wind directions are not directed from the active gypsum pile, but since they are an average direction over a 60 minute period, wind flow over the gypsum pile could have occurred a percentage of the time. King does not indicate the percentage of the total time flow was actually over the active gypsum pile, therefore the relative contribution or effect of the gypsum pile on ambient levels at the samplers cannot be estimated. It is also noted that for pond 20, the locations of the gypsum pile, gypsum pond, and Sampler 01 (Figure 4.13) indicates that particulate and gaseous fluoride from the pond 20 active gypsum pile could contribute to fluoride concentrations at the samplers whenever the pond contributed to the measured concentration, i.e. when the wind was directed from pond 20 towards Sampler 01.

Certain pond 20 data were also deleted in verification of the simulation model. Sixteen (16) one-hour time periods at Sampler 02 were removed from consideration because high fluoride values were measured

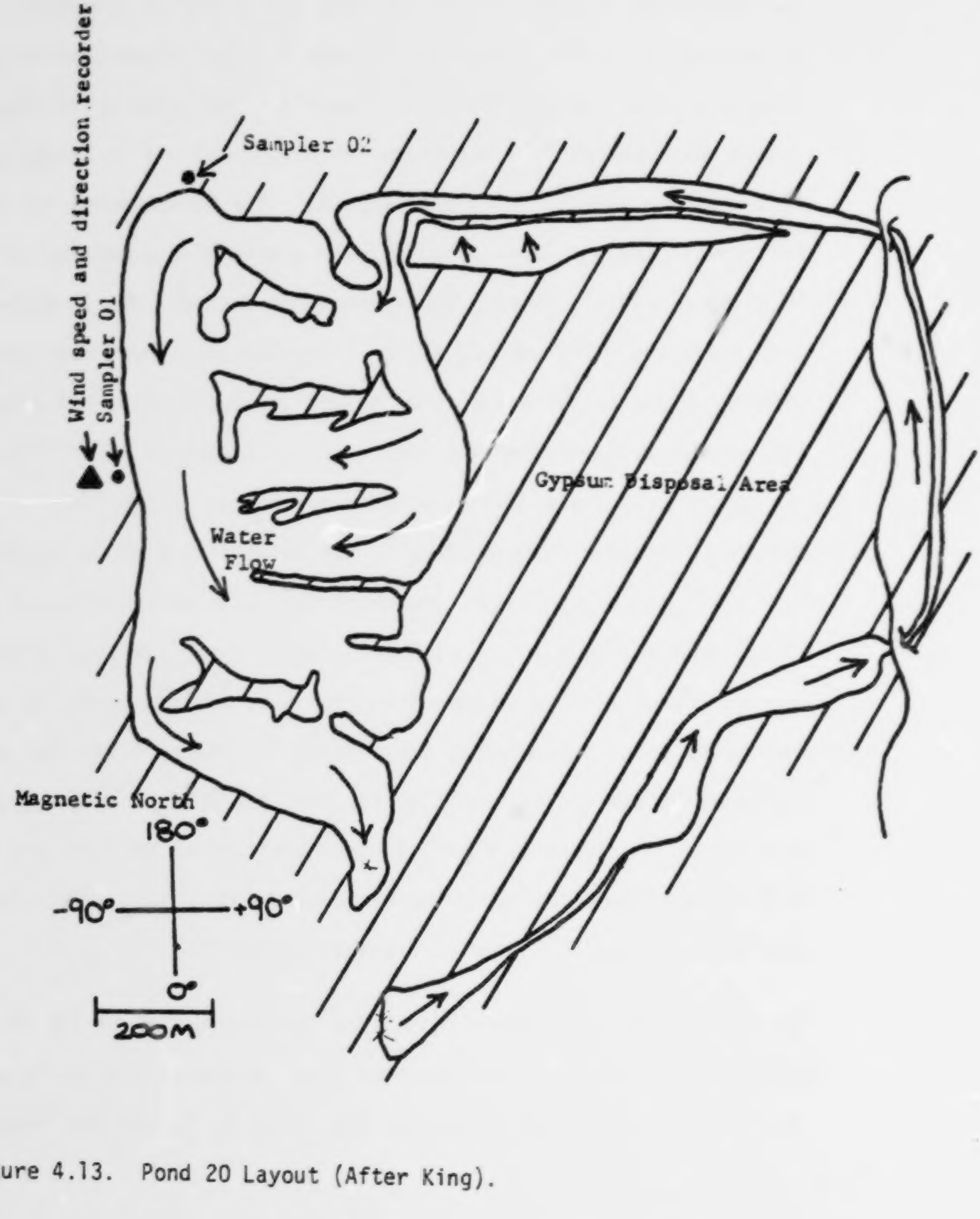


Figure 4.13. Pond 20 Layout (After King).

during these time periods. Calculated values were much lower than measured fluoride values. The explanation was given that some action by the phosphate plant in the gypsum disposal area caused the high ambient air concentrations. Sampler 01 displayed no similar increase. However, due to the locations of the samplers, the gypsum pond and the gypsum disposal area, it is likely that any activity in the disposal area affecting Sampler 01 would also affect Sampler 02. It is also likely that the gypsum pile would contribute to the fluoride measured at the samplers when the wind was such that the pond would also contribute. Since no upwind measurements were obtained, no estimate of the background gaseous and particulate fluoride contribution can be made.

Certain other data were also deleted from the pond 20 verification when model calculated concentration estimates were higher than measured values (see Appendix 15.5.4 of King's work). Justification is given that the model could not satisfactorily predict concentrations during conditions of strong solar insolation and low wind speed. This is a possible explanation, but not the only explanation. The measured and estimated concentration values were in good agreement ($r = 0.73$, d.f. = 9; significant at 95 percent confidence level), and certainly agreed within the experimental error and uncertainties inherent in the simulation model. It is questionable, then, that these data should not be used in the model verification.

King's conclusion that background sources of fluoride (i.e., sources other than the pond) did not contribute significantly to measured fluoride values at the samplers is not substantiated by the data. Only a limited number of background measurements were obtained: six at pond 10 and three at pond 20. This limited data is not sufficient to make any definitive conclusions on background concentrations. In addition, since King concluded that background fluoride levels were insignificant, no background measurements were made when the model validation data was gathered. Thus, it is impossible to assess the exact contributions of background fluoride to the total measured concentrations.

Pond 10 background estimates were obtained from one sampling station. The measured background values ranged from 0.0 to 0.92×10^{-6} gm-moles/m^3 fluoride and averaged 0.36×10^{-6} gm-moles/m^3 (Table 4.3). The average measured fluoride concentration obtained at pond 10 for the study was 3.12×10^{-6} gm-moles/m^3 and concentrations ranged from 0.64×10^{-6} to 10.48×10^{-6} gm-moles/m^3. These data indicate that background fluoride could contribute on the average 12 percent ($0.36 \div 3.12$) to measured fluoride levels at pond 10, which is indeed significant.

Three purported background measurements were obtained at pond 20. All of these measurements were made when calculations showed that the pond contributed insignificantly to the fluoride concentration at the sampler, i.e., when the average wind direction was not directed from pond to sampler. However, the same sampling locations were used in measuring the fluoride concentration when calculations with the simulation model showed the pond contributed significantly to the fluoride at the sampler.

Table 4.3. Measured background ambient fluoride concentrations and simulation model estimates.

	Measured Fluoride Concentration	Calculated Fluoride Concentration Due To Pond Emissions (x 10^{-6}g-moles/m^3)	Background Fluoride Concentration From Unaccounted Sources
Pond 10	0.0	0.0	0.0
	0.0	0.0	0.0
	0.0	0.0	0.0
	0.92	0.0	0.92
	1.06	0.30	0.76
	0.68	0.0	0.68
	0.20	0.03	0.17
Pond 20	0.53	0.0	0.53
	0.37	0.0	0.37

Thus, no upwind background measurements were made when the wind was blowing from the pond toward the samplers. This is very disturbing since the gypsum disposal area would be upwind of the pond and samplers under these conditions, and could contribute to gaseous and particulate fluoride levels at the sampling locations. It is also disturbing since the author concluded for pond 10 that the active gypsum pile there contributed significantly to fluoride levels near the pond. From these observations it must be concluded that background fluoride concentration could not be specified with any degree of confidence for pond 20.

To obtain a better degree of confidence as to the performance of the simulation model, all of the pond 10 and pond 20 measurements were plotted on a scatter diagram of calculated and measured fluoride concentrations (Figure 4.14 and Figure 4.15). The pond 10 data, when including all of the deleted observations, results in a significant correlation ($r = 0.85$, d.f. = 69) at the 1 percent level of significance. Thus, it can be stated with 99 percent confidence that a linear relation does exist between the measured and calculated values. The variation in the data due to uncertainties and errors in the simulation model is equal to $1-r^2$. For pond 10, this unexplained variation accounts for 28 percent of the total variation in the data. Linear regression analysis of all of the pond 20 data resulted in a poor correlation ($r = 0.15$, d.f. = 60). Thus, a linear relationship does not exist between the measured and calculated concentrations for pond 20.

Ninety-eight (98) percent of the variation in the data cannot be explained.

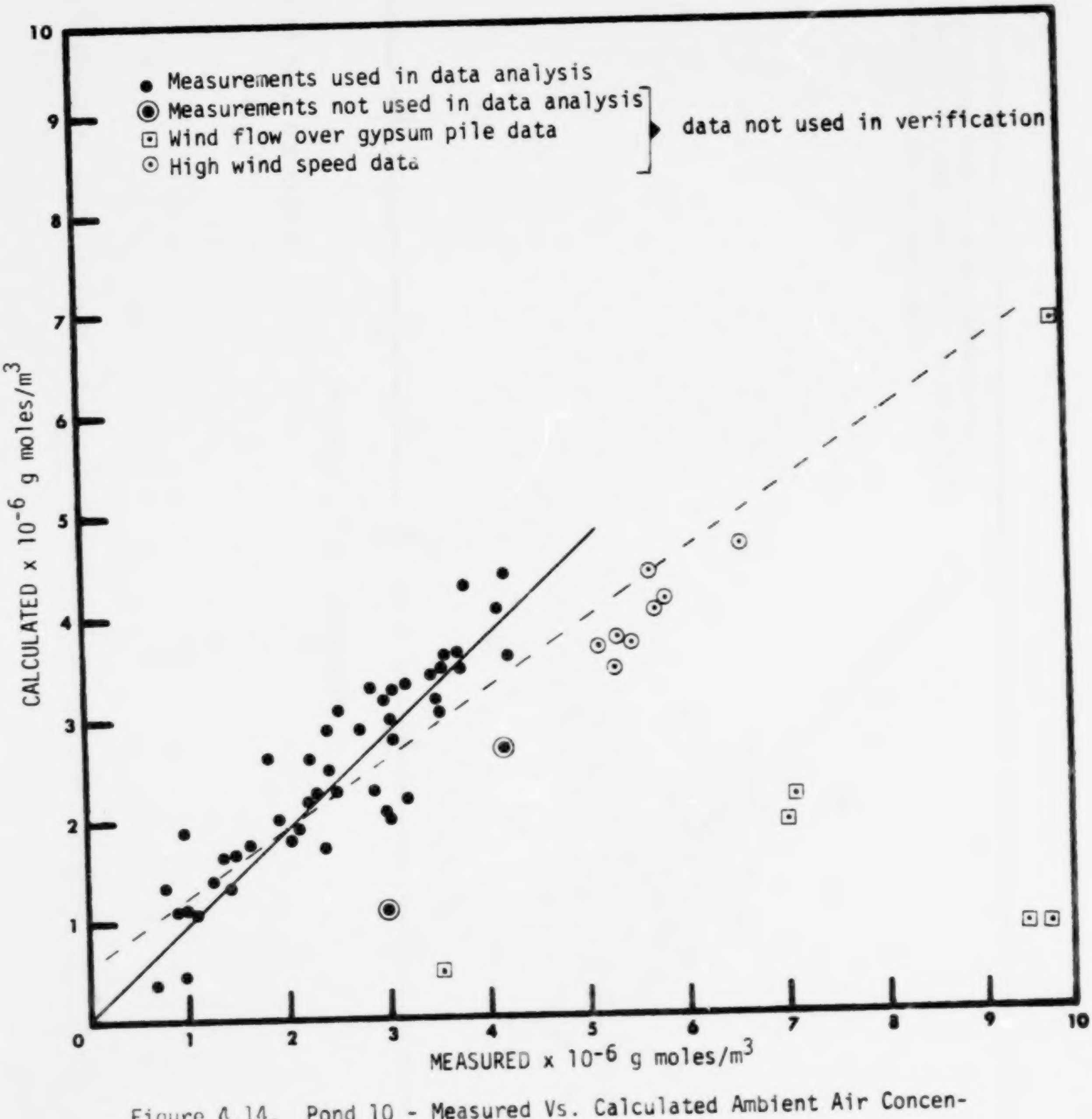
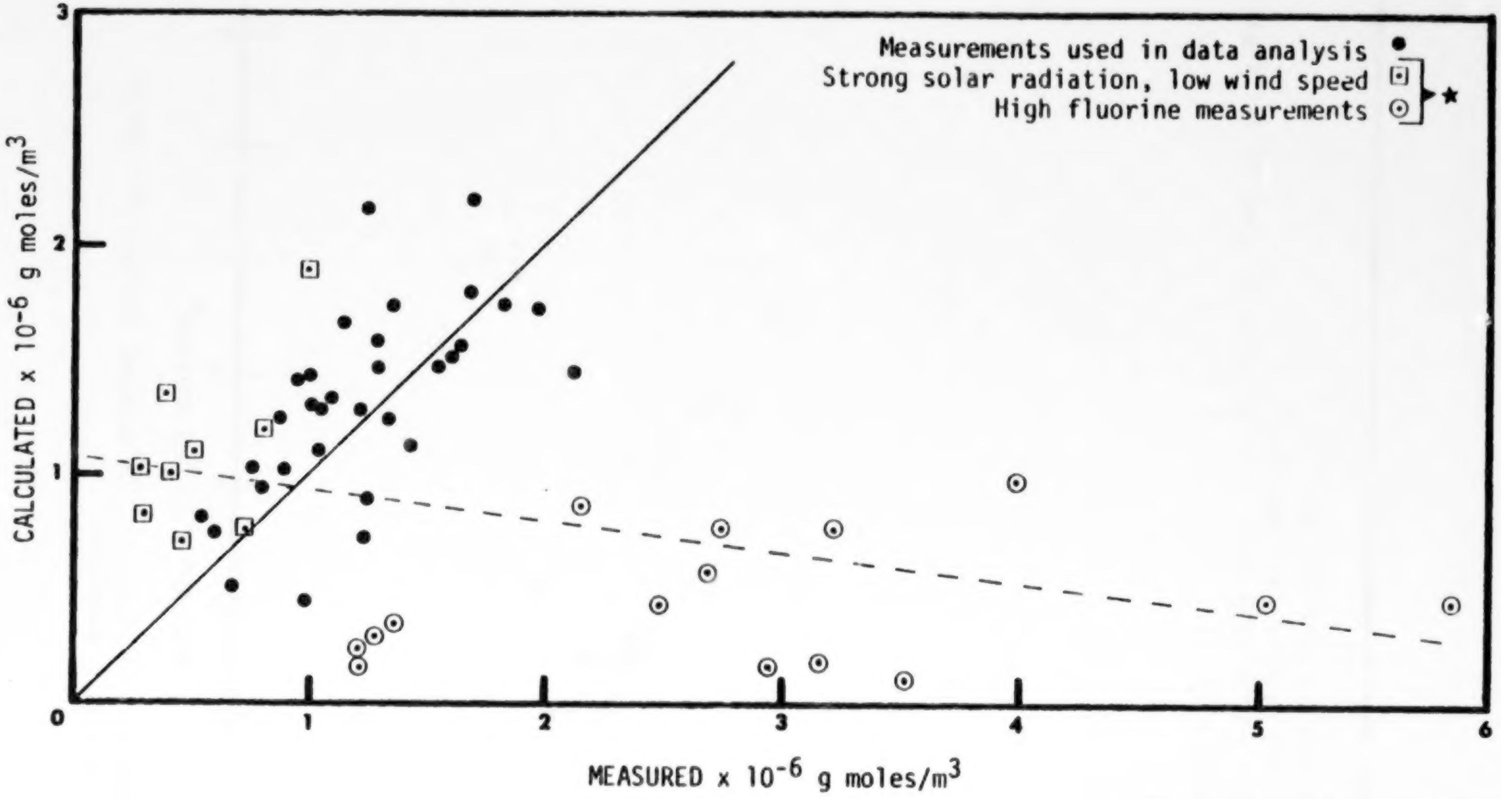


Figure 4.14. Pond 10 - Measured Vs. Calculated Ambient Air Concentrations at Samplers.



★ Data not used in verification

Figure 4.15. Pond 20 - Measured Vs. Calculated Ambient Air Concentrations at Samplers.

4.3.5.5 Verification of King's Simulation Model

The preceding discussion has alluded to many sources of uncertainty and error associated with the application of King's simulation model of gypsum pond emissions and dispersion. These uncertainties are not uncommon in verification and calibration of other dispersion models, and it is often difficult to obtain a good correlation between observed and model calculated values. Very rarely is a one-to-one correspondence between measured and predicted values obtained. As sampling time decreases, however, it is expected that calculated concentrations will more closely approach measured concentrations in magnitude. This is true since the variability of the parameters describing the atmospheric phenomena is decreased for shorter sampling times. In this respect, King's model is superior in that sampling times were very short (10 minutes).

Contrary to King's statement that a simulation model is accurate only if a one-to-one correspondence between measured and calculated values is satisfied (calculated = 1.0 x measured), any linear relationship between the two is accurate if the correlation is statistically significant, or if the model predicts concentrations within some defined confidence limits. Dispersion models typically overcalculate observed concentrations. Overcalculation results from model assumptions of steady-state conditions for emissions and meteorological parameters.

Elevated point source models have been found to overcalculate concentrations by a factor of 2 to 10. This in itself, however, does not invalidate the model.

Dispersion models cannot be used to validate parameters used as inputs to the model. This is because our imprecise knowledge of atmospheric phenomena does not insure that the dispersion of emissions into the atmosphere is being correctly or completely simulated. In this respect, verification of a dispersion model does not verify an emission factor, for the emissions could be in error by a proportionate amount, and verification of the model still obtained. (For instance, the slope of the linear regression line would change). It is imperative that before a dispersion model can be properly verified, the pollutant emissions must be known.

In conclusion, the analysis of King's modeling work points up the following major shortcomings:

1. Verification or calibration of a diffusion model for fluorides does not substantiate an emission factor for fluorides.

2. Several measured concentrations were deleted from analysis but seemingly lacked justification for such removal.

3. Background concentrations of fluoride could not be estimated based on the available data obtained during the study.

4. Since background concentrations were not available, the contribution of fluoride from the gypsum ponds and that from other sources of fluoride could not be delineated.

5. Based on 1-4 above, a reliable emission factor for fluorides from gypsum ponds has not been substantiated.

4.4 COMPARISON OF EMISSION FACTORS FROM THE LITERATURE

Since Cross' and Ross' study provided no useful data regarding an emission factor, it will not be considered in this section. As stated in Section 4.2.3, Tatera measured wind speed in a wind tunnel at a point 0.1 meters above the water. It is important to note, first of all, that the velocity distribution in the wind tunnel is such that the velocity will approach zero at all four walls due to surface friction. As Tatera stated, there are no accepted hydrodynamic scaling parameters which allow wind tunnel results to be applied directly in large scale systems. The velocity profile above a pond generally follows a logarithmic distribution. It is zero at the surface and increases with height.

Nevertheless, in order to make a comparison of the two studies, a relationship, empirically developed by King, was used to scale Tatera's velocities to a height of 16 meters.

$$\frac{V_1}{V_2} = \frac{Z_1}{Z_2} \exp\left[0.2909 + 0.06154\,(L) - 0.01164\,(V_{16})\right] \qquad (4.38)$$

where:

V_1 = wind speed at Z_1 (0.1 meter)

V_2 = wind speed at Z_2 (16 meters)

L = measured lapse rate (between 2 and 16 meters)

V_{16} = wind speed at 16 meters

Comparisons of emission factors as determined by King and Tatera (incorporating the correction above) are presented in Table 4.4 for three temperatures. Comparisons at 75°F and 85°F are not readily applicable since most gypsum ponds operate at temperatures above 90°F. Typically, process waters enter the pond at 115°F and are returned to the process at 95°F. Unfortunately, Tatera obtained all of his data between 75°F and 95°F, while King conducted vapor pressure studies between 70°F and 100°F. It would have been far more useful to have obtained data between 85°F and 115°F.

Tatera's emission estimates at 95°F are approximately a factor of 2 greater than those of King. In accordance with our previous discussion, a judgement cannot be made as to the validity of either method of estimation when applied to a particular gypsum pond. It can be argued from purely physical chemical grounds that the emission rate should be about one-fifth the values determined by King*. Thus, the best statement

---

* Special communication with Dr. Alonzo Coots of International Industrial Consultants; based upon assumption of saturated calcium sulfate with calcium fluoride controlling free fluoride levels found in gypsum ponds. Attempts to verify these assumptions in the laboratory were confounded by the complexity of the solution.

Table 4.4. Comparison of Emission Factors Predicted by King and Tatera at Various Temperatures.

V_{16} M/Sec	EMISSION FACTOR IN LB/DAY-ACRE		
	1	2	4
V_1 M/Sec	0.25	0.54	1.2
Ft/Min	50	106	238
75°F			
King (Pond 10)	0.96	1.6	2.9
Tatera (Process Water)	0.41	0.86	1.9
85°F			
King	0.75	1.3	2.2
Tatera	0.52	1.1	2.4
95°F			
King	0.92	1.6	2.8
Tatera	1.5	3.2	7.3

that can be made at this point is that the characteristic emission factor appears to lie in the range of 0.1 to 10 lb/acre-day and that a careful field study would seem appropriate to determine the contribution of volatile fluorides from the ponds to the atmospheric fluoride levels around the ponds.

5.0 DETERMINATION OF GASEOUS FLUORIDE CONCENTRATIONS IN THE VICINITY OF A GYPSUM POND

In order to estimate concentrations it was necessary to assume a typical gypsum pond, servicing a phosphoric acid plant, producing 1,000 TPD of P_2O_5. Secondly, since no accurate or reliable emission rate is known, downwind χ/Q isopleths were calculated. Concentration isopleths can then be calculated as a function of an assumed emission factor.

5.1 DESCRIPTION OF TYPICAL GYPSUM POND

The gypsum pond is an integral part of a typical phosphoric acid plant. It serves as a receptacle for wastewater which during the manufacturing process comes into direct contact with raw materials, intermediate products, by-products, waste products or finished products.

Gypsum pond water is recirculated to the phosphate processes and used mainly in scrubbers, barometric condensers, and for slurrying waste gypsum. After settling of gypsum solids in the ponds, the water is allowed to cool by evaporation and reused.

Figure 5.1 shows the configuration of the "typical" gypsum pond. Process waters enter at about 115°F. The area around the entry point would, therefore, be the area for maximum evaporation and fluoride emission. The water cools by evaporation down to about 95°F which is the temperature at which it reenters the process. A recirculation rate of 30,000 GPM would be expected.

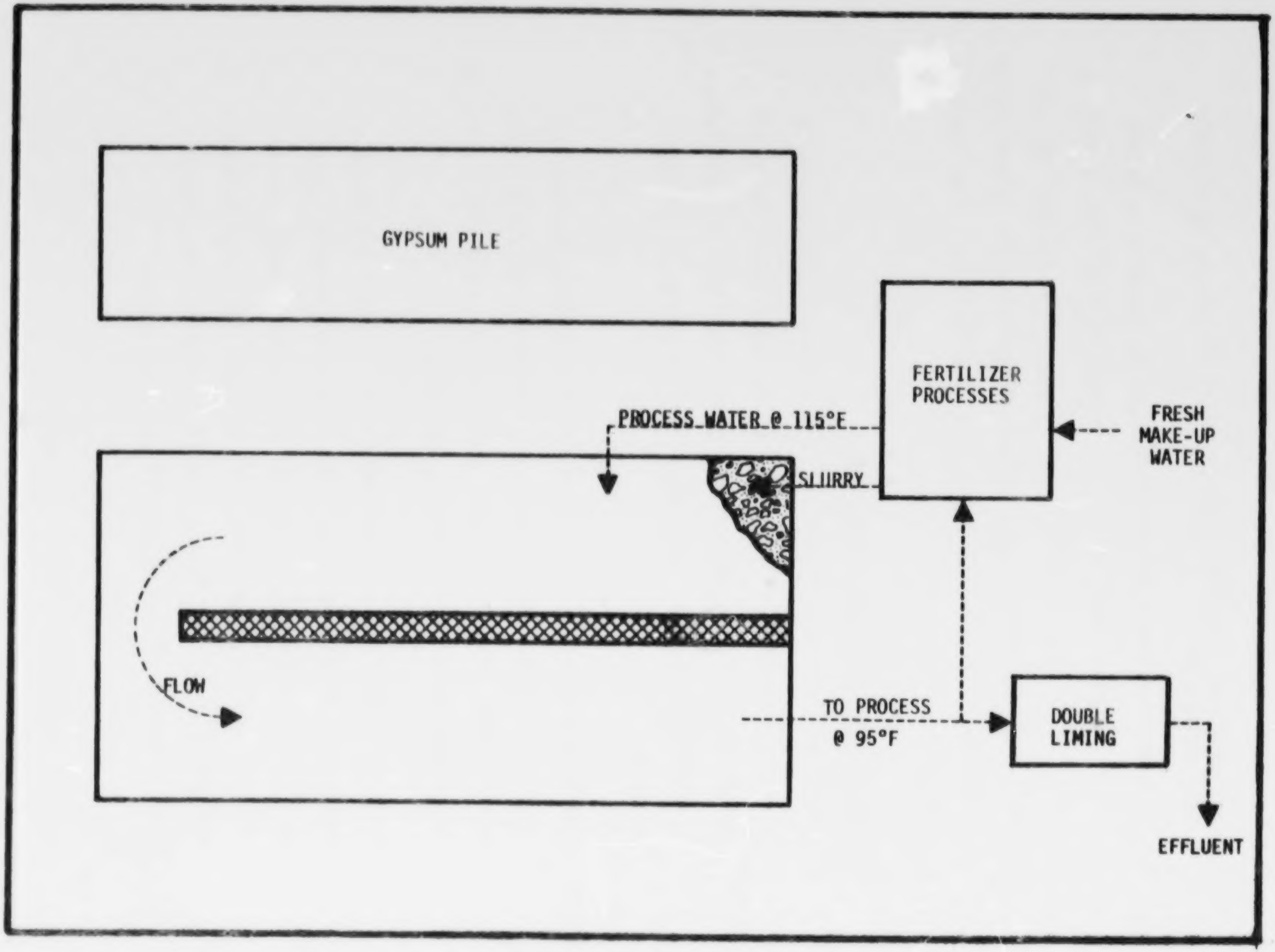


Figure 5.1· Typical Gypsum Pond Servicing A 1000 TPD-P_2O_5 Plant.

The average concentrations of species in gypsum pond water are summarized below. These figures are based on the mean measurements from thirteen ponds provided by The Fertilizer Institute.

Species	Concentration (mg/l)
Al	170
Ca	1600
Cl	3500
F	5100
Fe	210
K	110
Mg	165
Na	930
NH_3 - N	520
P	4500
SO_4	4400
Si	1560
pH	1.6

The important factors to be considered and the concentrations of free fluoride ions (F-), pH and temperature. The value for fluorides given above are not free fluoride measurements, but are total soluble fluoride. These three factors should be sufficient to specify an equilibrium vapor pressure for HF in the pond water, which is directly related to the emission factor.

A typical gypsum pond, handling both slurry and process water from a 1,000 TPD-P_2O_5 plant would have about 350 acres of wet area. Water depth would be about 10 feet. Most likely it would be located adjacent to the plant and surrounded by mined out land of sparse vegetation or swamp. Assuming that the pond is used for both gypsum settling and cooling, there would be a region where the stream from the sluicing operation would join the pond. This area, known as the gypsum flats, is where the gypsum settles. It would constantly be worked by draglines which would remove settled wet gypsum and transfer it onto an active gypsum pile to dry. The gypsum pile would be about 80 feet high on about 150 acres adjacent to the wet pond.

When rainfall exceeds evaporation, a certain amount of the water would be discharged from the pond. Prior to entering a water stream, it would be treated by double stage liming which would raise the pH to 9.0. This would effectively remove fluoride as fluorspar through a series of reactions. It would be necessary to use this system on an intermittent basis for 3 months per year.

5.2 GROUND LEVEL GASEOUS FLUORIDE CONCENTRATIONS IN THE VICINITY OF A GYPSUM POND

The Gaussian finite line source equation was used to estimate gaseous fluoride concentrations downwind of a hypothetical gypsum pond. A computer program was developed to calculate concentrations due to a large number of spatially distributed line sources at a number of downwind receptor points. The line source model was chosen for the area source simulation because it is considered the best available calculation technique.

A 350 acre rectangular pond, similar to the configuration shown in Figure 5.1, was chosen for simulation. The pond's length was taken to be twice its width. The pond was divided into a number of equal sections, 10 meters wide. A line source was placed at the center of each segment oriented cross-wing, and the segments emissions concentrated into the line source contained therein.

Estimations of ground-level fluoride concentrations were obtained for two different meteorological situations (typical average day conditions and worst conditions). Isopleths of concentration/emission rate (χ/Q) ratios were obtained for each situation (Figure 5.2 and Figure 5.3). Average conditions consisted of stability class 1 and a wind speed of 3 m/sec. Typical worst conditions consisted of stability class 6 and a wind speed of 2 m/sec. The χ/Q value gives the normalized ground-level concentration in relation to the emission rate. For example, if the χ/Q ratio is 1.0, the ground level concentration will be equal to 1 $\mu g/m^3$ if the emission rate is 1 lb/acre/day. If the emission rate is 10 lb/acre/day and χ/Q is equal to 1.0, the ground-level concentration would be 10 $\mu g/m^3$.

The concentrations predicted by the simulation line source model should not be construed to represent actual concentrations which would exist downwind from a real gypsum pond. Verification and calibration of the model is required before it can be confidently used to predict concentrations near gypsum ponds. The greatest utility in the present simulation is in the ground-level concentrations patterns generated by the mode. For meteorological conditions similar to those used in obtaining Figures 5.2 and 5.3, the patterns shown are expected to be similar to those actually occurring near the pond. However, the magnitude of the concentrations may not be those displayed.

The simulation assumes a typical gypsum pond as described previously, and assumes a constant wind velocity, unaffected by topographic

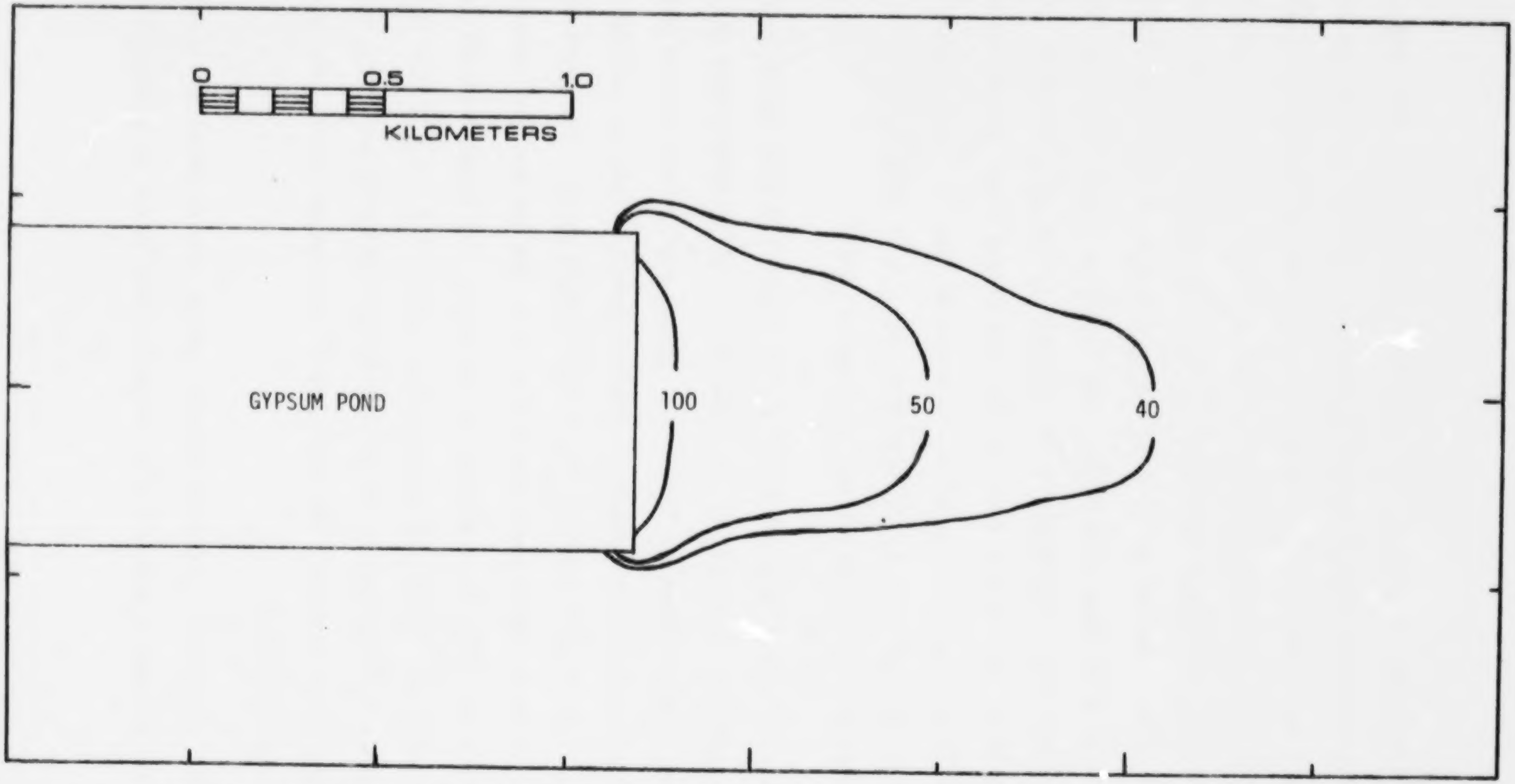


Figure 5.2 Isopleths of Calculated Ground-Level Fluoride x/Q Ratios Downwind of a Hypothetical Gypsum Pond. (Stability Class 6, Wind Speed = 2 m/sec.)

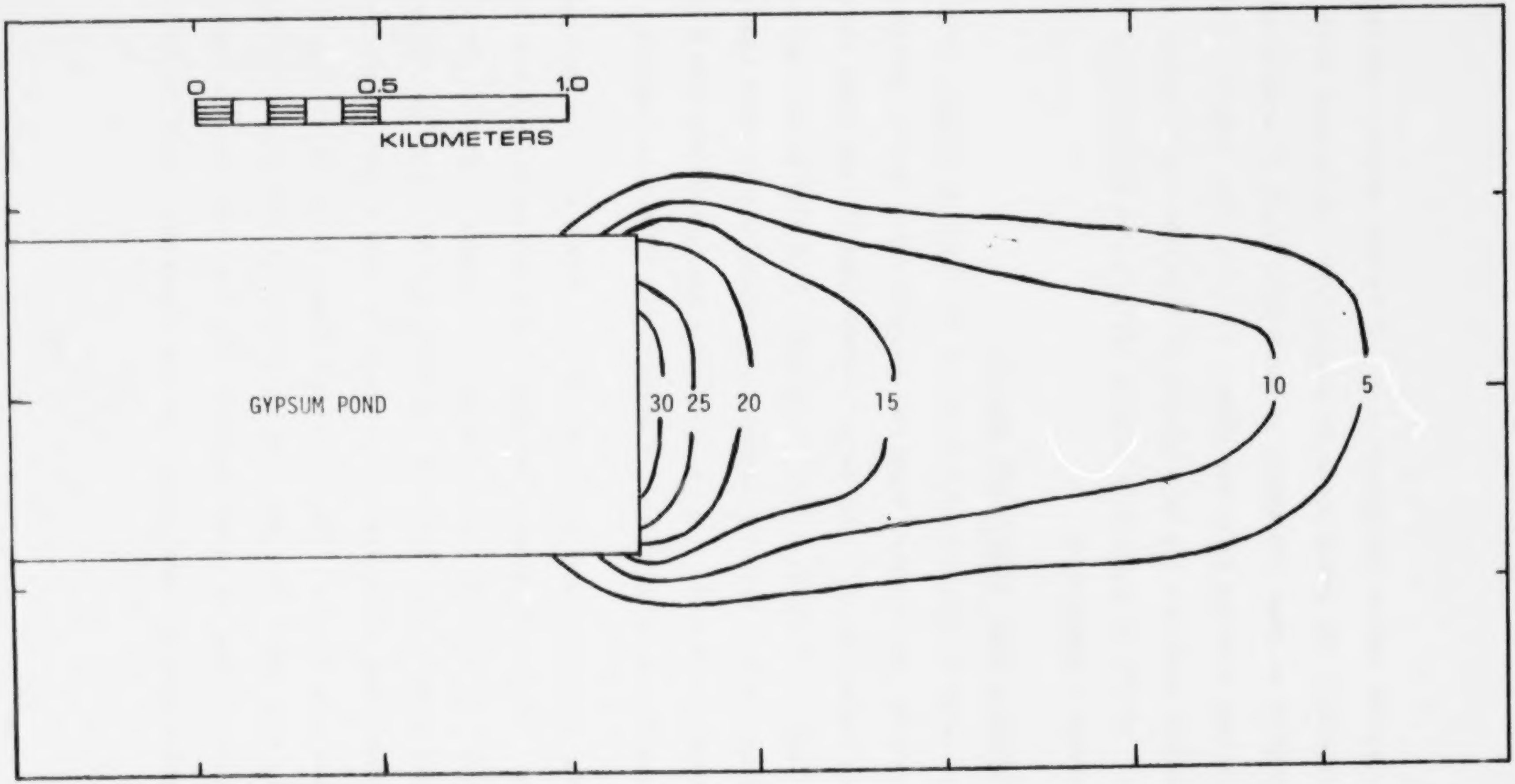


Figure 5.3 Isopleths of Calculated Ground-Level Fluoride x/Q Ratios Downwind of a Hypothetical Gypsum Pond. (Stability Class 4, Wind Speed = 3 m/sec.)

features such as the gypsum pile. It further assumes contributions from only the gypsum ponds in gaseous form. Background levels would have to be known and added, as would particulate or gaseous contributions from the piles and plant. If it is true, however, that gypsum ponds are the main sources of fluorides, then Figures 5.2 and 5.3 should be accurate in showing the relative dispersion of fluorides around a gypsum pond.

5.3 COMPUTER MODEL SENSITIVITY ANALYSIS

In order to test the sensitivity of the model to changes in line source spacing, the computer model was executed for a typical gypsum pond configuration utilizing various meteorological conditions and downwind receptor distances. Each of the ponds King studied were approximately 500m x 900m. Fluoride samples were located within about 100m of the edge of the ponds. In his simulation model, King employed a 10m line source spacing to calculate downwind fluoride concentrations.

For comparison purposes, a gypsum pond 500m x 840m was employed for the sensitivity study. The mean wind direction was situated crosswind (90°) of the 840m sides. Concentrations were calculated for receptor distances of 10m, 25m, 50m and 150m, and for a range of meteorological conditions. Calculations were made for both a 10m line source spacing and a 5m spacing. The results are tabulated in Table 5.1. Examination of this table indicates that the effects of line source spacing are most critical at closer receptor distances, but are also dependent on meteorological conditions. For the parameters listed in the table,

Table 5.1 Sensitivity Analysis for the Finite Line Source Model

Meteorological Conditions		Fluoride concentration ($\mu g/m^3$)							
		Line Source Spacing = 10m				Line Source Spacing = 5m			
		Receptor Distance (m)				Receptor Distance (m)			
Stability	Wind Speed (m/s)	10	25	50	150	10	25	50	150
1	3	0.9	0.7	0.5	0.4	0.8	0.7	0.5	0.4
3	5	1.1	0.9	0.7	0.5	1.0	0.8	0.7	0.5
4	1	8.5	7.0	5.8	4.5	8.1	6.8	5.7	4.5
4	10	0.8	0.7	0.6	0.5	0.8	0.7	0.6	0.5
5	3	3.7	3.1	2.6	2.1	3.6	3.0	2.6	2.1

the largest difference between conditions calculated using 10m and 5m line source spacings is 0.4 μg/m^3 (stability class 4 and wind speed of 1 m/sec). This value represents only a 5 percent difference in the calculated concentration. Based on the sensitivity analysis, it is concluded that a 10m line source spacing, such as that employed by King, will introduce a certain small error in the calculated concentrations, but that a 10m spacing results in sufficient accuracy for model validation/calibration purposes.

6.0 IDENTIFICATION OF CONTROL TECHNIQUES

Several control processes for reducing fluoride emissions from gypsum ponds are evaluated in this section. All of the candidates examined are unusual with respect to air pollution control equipment in that they are indirectly applied to the air emissions. In general, air pollution control equipment includes mechanical collectors, bag filters, electrostatic precipitators, and scrubbers. It is not surprising to find special problems associated with the processes considered herein due to the complex chemistry involved in the pond waters, the large water volumes involved, and the acidic nature of the fluorides themselves.

A search of the literature and discussions with members of the phosphate industry and the EPA revealed six potential candidates. They are:

1. Kidde Process for treating barometric condenser and scrubber water.
2. Swift Process for treating barometric condenser and scrubber water.
3. Liming the gypsum pond water to raise the pH and produce insoluble calcium fluoride.
4. Dry conveyance of the gypsum to waste stacks instead of sluicing with water.
5. Calcining the rock prior to treatment in the process.
6. Changing the basic process to the Hemi/Dihydrate process for phosphate production.

In addition to these six processes, consideration is given to complete segregation of the gypsum and cooling ponds. This segregation is considered tantamount in applying any of the first four control options;

therefore a brief discussion will follow concerning the benefits to be derived from a two pond system.

Two Pond System in a Phosphoric Acid Plant

Phosphoric acid plants utilize a wide range of gypsum/cooling pond arrangements. In most cases process and gypsum sluicing waters are transported to a common pond allowing these waters, which are vastly different in properties to mix, with the ultimate result that both process and gypsum pond waters will be highly contaminated with acidic P_2O_5, H_2SO_4, as well as H_2SiF_6.

In some cases, separate cooling and gypsum ponds are utilized. All process waters except gypsum sluicing water are sent to evaporative cooling ponds. Gypsum slurry is pumped from the filtration operation to a gypsum pile where the gypsum settles. The supernatant water is subsequently recycled through the cooling pond, thus contaminating it with P_2O_5, H_2SO_4, and fluorides from the filtered gypsum.

A third possible method involves employing a "Two Pond System" in which the cooling pond can not be contaminated with waters from filtration. This method was discussed by Parish and Enriquez in a recent paper (1973). It was recommended as part of a two-step solution for reducing fluoride emissions from gypsum and cooling ponds to be used simultaneously with the "Swift Absorption Process".

The reasons for separate ponds were given by Enriquez and Parish were:

1. The required size of the gypsum slurry pond is small (about 5 acres) since no area is required for cooling. This water would be the most contaminated and acidic water in the plant due to the presence of P_2O_5, H_2SO_4, iron and aluminum complexes, and fluorides from the filtration operation.
2. The size of the pond required for the barometric condensers is determined by the cooling duty requirements. This area is estimated to be 0.1 acre/TPD P_2O_5 .

Since the cooling pond will receive condensed vapors from the flash cooler and evaporators, it is possible that entrained phosphoric acid could be present as a contaminant. This, however, may be minimized by the addition of entrainment separators, the result being that the main contaminant entering the cooling pond will be limited to fluorides.

Figure 6.1 schematically shows the proposed system. One pond would service the filtration operation by receiving gypsum slurry. The other pond would receive waters from the fume scrubbers, flash coolers, and the evaporation trains. The cooling pond will require about 200 acres for a 1,000 TPD P_2O_5 plant, while the gypsum pond will require approximately 5 acres.

The costs required to segregate the two ponds at an existing plant are site specific, but are considered negligible compared to the other control costs presented herein. Since each plant will have different problems

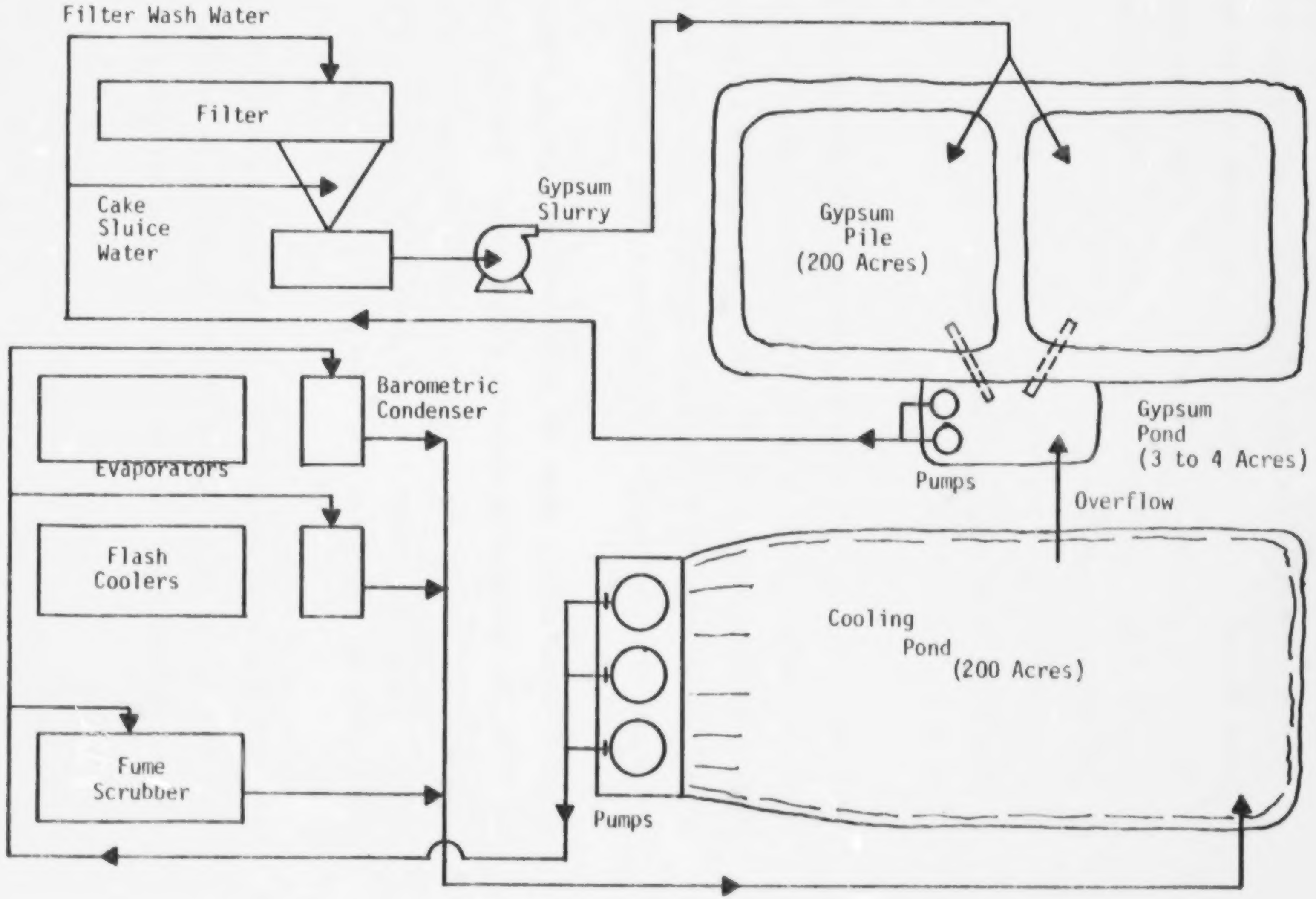


Figure 6.1. Two Pond System for Phosphoric Acid Plant.

switching to a two pond system, costs have not been calculated. These costs, however, are expected to be well below the cost of the fluoride control equipment.

Judging the cost-effectiveness of each process was facilitated by using the following criteria:

1. Ability of the process to lower gypsum and cooling pond emissions (efficiency)
2. Total capital investment requirements
3. Cost per ton of P_2O_5 produced
4. Commercial availability
5. Demonstrated capability

Our findings regarding cost and efficiency are summarized in Table 6.1. Examination of this table reveals a large range of control costs (\$1.25 to \$7.46 per ton P_2O_5) and efficiencies that warrant some discussion.

The Swift Process is, in this study's estimate, the most cost-effective method for control of emissions from gypsum and cooling ponds when employed in conjunction with a segregated two pond system. A saleable product (H_2SiF_6) is recovered. The product is sold to large municipalities for fluoridation of water at approximately \$200/ton H_2SiF_6 (delivered) and to aluminum companies for production of fluorosilicates and other fluorine compounds used in processing aluminum at \$60/ton H_2SiF_6 (FOB Plant). The economics of this process are considerably improved if all of the fluosilicic acid produced is sold at the latter price.

Table 6.1. Capital Investment and Operating Costs For Fluoride Control of 1,000 TPD P_2O_5 Plant.

Process	Where Applied	Fluorine Removal Efficiency	Total Capital Investment $MM	Annualized Operating Costs Total, MM	Annualized Operating Costs $/Ton P_2O_5	By-Product
Kidde	Barometric Condensers	95-98%[a]	2.57	2.31	$ 7.46	$(NH_4)_2\ SiF_6$
Swift Absorption	Barometric Condensers	90%[b]	1.30	0.17	1.25[c]	H_2SiF_6
Liming	All Cooling Pond Water	90%[b]	2.10	0.97	3.13	None
Conveyor	Gypsum Filter After Acidulation	a	1.07	0.43	1.40	None
Pre-Calcination of Rock	Crushed Phosphate Rock	b	29.81	7.57	24.42	None

a) Not calculated due to uncertainties in fluorides evolved from filter cake.

b) 90% removal of fluoride in rock is achieved. However, the fluorides evolved are scrubbed and transferred to ponds.

c) A credit of $2.26/ton P_2O_5 is realized if all fluosilicic acid produced is sold at $60/ton (100% H_2SiF_6).

In this case a credit of \$2.26/ton P_2O_5 may be realized. Although this study did not conduct a market survey, discussions with several individuals involved in the production and marketing of phosphates and aluminum lead the authors to believe the market for H_2SiF_6 can absorb some expansion, primarily in the aluminum industry.

The second most cost-effective method for reducing emissions involves liming the pond waters to a pH of about 4.0. This reduces emissions by lowering the fluoride vapor pressure. Unfortunately, this technique does not produce a saleable byproduct and is subject to serious limitations. Perhaps the most severe of these is the increased potential for equipment scaling caused by precipitation of silica. Current practice tends to eliminate this problem which has plagued the industry in the past. Additional problems arise from secondary impacts associated with the mining of limestone necessary for this control. While it is outside the scope of work for this contract to assess secondary environmental impacts outside of the phosphate complex, we feel it significant that approximately 37,200 tons per year of limestone will be required to lime the pond waters associated with a 1,000 TPD P_2O_5 complex.

The Kidde Process has the highest potential recovery of all candidates for fluorine in the weak phosphoric acid. Since it is believed that the fluorine from the barometric condensers is the primary source of emissions from the cooling pond, this process receives the highest technical merit. Unfortunately, the high annualized costs put this process at a severe disadvantage when compared with its nearest competitor, the Swift vapor absorbers. The high costs of the Kidde Process reflect the study's assessment that the process be limited to that required to control fluoride emissions. Thus, the byproduct in this instance is ammonia silicofluoride and not aluminum fluoride, as Kidde suggests. The limited market for the ammonia salt (ca. 2,000 TPY) renders this byproduct a waste stream rather than a saleable product. Regardless, it is the opinion of the authors that the increased process complexity and additional capital investment required to produce aluminum fluoride is unwarranted as a control scheme. Perhaps these are the very reasons why Kidde has been unsuccessful in marketing this process.

The other three processes (dry conveyance of gypsum, pre-calcination of the phosphate rock, and the hemi/dihydrate process) all suffer from the disadvantage that a major process change or change in industry practice is required. None of these three is currently used on a large scale in the U.S.

The remainder of this section is devoted to a detailed assessment of these six candidates regarding cost and effectiveness. In reviewing this section, the reader is reminded that these estimates have been derived from literature and other sources and not from detailed engineering estimates.

6.1 KIDDE PROCESS

6.1.1 Process Description

The Kidde Process, used to defluorinate wet-process phosphoric acid and convert the extracted fluorine into various fluorine compounds, is a patented process developed by Kidde Process Company, Pasadena, California. Fluorine compounds that may be produced include aluminum fluoride, synthetic cryolite (Na_3AlF_3), hydrogen fluoride, and synthetic fluorspar.

Figure 6.2 is a detailed process flow diagram of the Kidde Process for a 1,000 TPD P_2O_5 facility. The reaction sequence is as follows. Reactive silica is mixed with phosphoric acid as it is fed to the acid concentrators. The silica has been dried to about 10 percent moisture and is premixed with the raw 30 percent P_2O_5 acid in an agitated tank with about 15 minutes retention time. The amount of silica required is determined by the amount of fluorine in the raw acid. The resulting slurry is fed to the concentrators through the usual control system. The principal reaction at this point is:

$$SiO_{2(s)} + 4HF_{(aq)} \qquad SiF_{4(g)} + 2H_2O \tag{6.1}$$

The overhead vapors from the acid concentrators are now condensed with an aqueous ammonium bifluoride solution; the pH of this condensing solution is approximately 4.0. As currently practiced, these vapors are condensed with cooling water or weak fluosilicic acid with a pH of 1.5 to 2.0. Herein lies a major advantage of the Kidde Process. Scrubbing with the higher pH bifluoride solution produces condensed vapors with a lower fluoride vapor

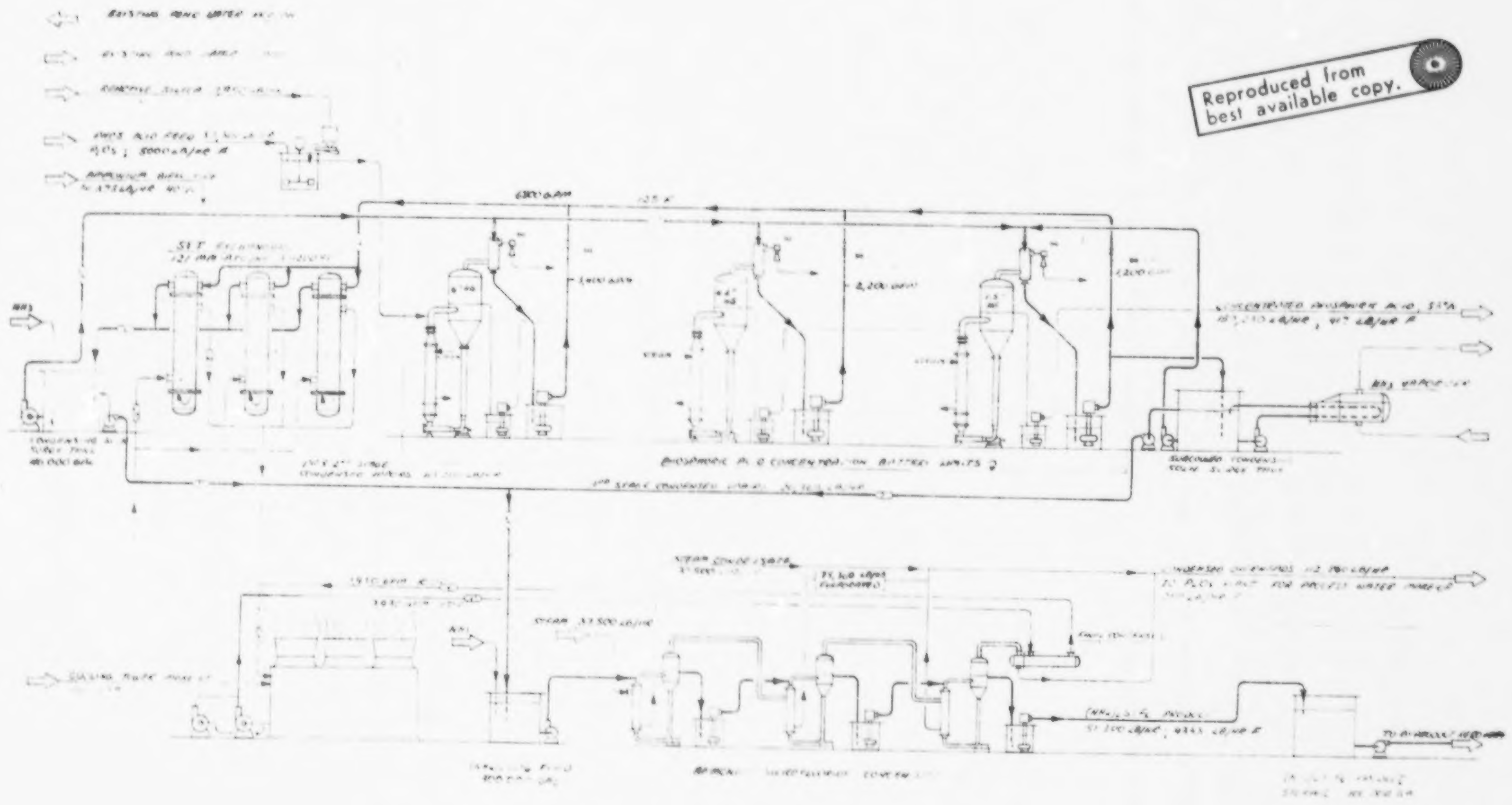


Figure 6.2. Kidde Closed-Loop Fluorine Recovery for a 1,000 TPD P_2O_5 Plant.

Reproduced from best available copy.

pressure. At this point, the condensed SiF_4 reacts with the bifluoride as follows:

$$SiF_{4(g)} + 2(NH_4)F \cdot HF_{(aq)} \qquad (NH_4)_2SiF_{6(aq)} + H_2SiF_{6(aq)} \tag{6.2}$$

In the next step of the Kidde Process, the condensed vapors from the various stages of evaporation are combined. This combined stream is then neutralized with ammonia which neutralizes the acid produced in the barometric condensors (eq. 6.2). This proceeds according to the following equation:

$$H_2SiF_{6(aq)} + 2NH_{3(aq)} \overset{\text{pH5}}{\quad} 2(NH_4)_2SiF_{6(aq)} \tag{6.3}$$

Concentration of the resulting solution is then achieved in multiple effect evaporators. The product, ammonium silicofluoride, is then stored for shipment or further reaction, as follows.

The product ammonia silicofluoride can be reacted further to produce additional products. An example of such a scheme is depicted in the following reaction scheme:

$$(HN_4)_2SiF_{6(aq)} + 4NH_{3(aq)} + 2H_2O \qquad 6NH_4F_{(aq)} + SiO_2\downarrow \tag{6.4}$$

$$2NH_4F_{(aq)} \overset{\text{heat}}{\quad} NH_4F \cdot HF_{(aq)} + NH_3\uparrow \tag{6.5}$$

$$6NH_4F \cdot HF_{(aq)} + Al_2O_3 \cdot 3H_2O_{(s)} \qquad 2(NH_4)_3AlF_6\downarrow + 6H_2O \tag{6.6}$$

$$(NH_4)_3AlF_{6(s)} \overset{900°F}{\quad} AlF_{3(s)} + 3NH_4F\uparrow \tag{6.7}$$

This scheme is that recommended by Kidde to produce aluminum fluoride which can be marketed to the aluminum industry. It has added advantages in that the silica and ammonia are recovered; these can then be recycled to the P_2O_5 plant for further use.

For the purposes of this study, reactions 6.4 through 6.7 are not incorporated in the fluoride recovery scheme. This is because the emission reduction estimated in the following section is effected by reaction 6.1 through 6.3; i.e., removal of fluoride from recyclable process waters is achieved at that point.

6.1.2 Process Applicability for Fluoride Emission Reduction

The applicability of this process as a candidate for reducing fluoride emissions from gypsum ponds is due to the lowering of the fluoride vapor pressure through neutralization with ammonia. An estimate of the emission reduction potential is arrived at as follows. As currently practiced with no fluorine recovery, the overhead vapors are condensed with recycled cooling pond water; the pH of this solution is approximately 1.5 to 2.0. At this pH, the fluoride vapor pressure is approximately 13.8×10^{-6} mmHg (25 C) (HEW, 1970). In the Kidde Process, condensed vapors are not sent to the cooling pond as in the above scheme. Instead, the solution is concentrated and neutralized to a pH of 5.0. At this pH, the fluoride vapor pressure is only 0.65×10^{-6} mmgHg (25 C). Therefore, in the final condensor of the ammonium silicofluoride evaporation train, the vapor pressure is approximately reduced by the following amount:

$$\text{Approximate fluoride reduction} = (13.8 - 0.65) \times 100\%/13.8 = 95.3\%$$

This is approximately the emissions reduction to be expected since the ammonium silicofluoride evaporation train operates at this pH which is why the fluorine content of the product stream is less than 0.2% F. (Figure 6.2).

6.1.3 Process Evaluation

In April, 1974, the Kidde Process Company submitted a technical and economic study to Shahpur Chemical Co. Ltd. of a proposed fluorine-recovery and aluminum fluoride-manufacturing installation at the company's phosphate plant at Bandar Shahpur, Iran. The study predicts costs of less than \$10.00 per ton for extracted fluorine and less than \$100.00 per ton for aluminum fluoride. The selling price for aluminum fluoride at that time (1974) was over \$300.00 per ton. However, no full-scale plant actually exists today, or is currently under construction.

Adaption of a fluorine-recovery system to an existing wet-process phosphoric acid plant should present few problems. The major items of equipment that must be added are the triple-effect evaporators for ammonium silicofluoride concentration, the shell and tube heat exchangers used for cooling the condensed overhead products, and a small cooling tower for removing heat associated with the ammonium silicofluoride evaporators (see Figure 6.2).

The existing barometric condensors used in concentrating the P_2O_5 can be used with the Kidde Process since the condensing medium (ammonium bifluoride) is less corrosive than the currently used pond waters.

Additional benefits that should result from installation of the Kidde Process include:

1. Reduction or elimination of liming for pond water discharged from the plant's cooling ponds.
2. Improvement in the physical properties of the phosphoric acid due to a reduction in its fluorine content.
3. Increased recovery of fluoride otherwise lost in the evaporation stage.

Of these, the third was estimated in Section 6.1.2. The first two are not easily quantifiable; i.e., it is not easy to assess cost benefits associated with them. However, both of these are benefits that should be attainable with this system.

6.1.4 Process Economics

Estimated incremental capital investment requirements and annualized operating costs for a 1,000 TPD phosphoric acid facility are summarized in Tables 6.2 and 6.3, respectively.

The data were determined in the following manner. Equipment sizes recommended by Kidde for a 560 TPD P_2O_5 plant were examined for reasonableness. These sizes were then adjusted to process the flows corresponding to a 1,000 TPD plant. Costs for major equipment items were obtained from published sources; standard engineering estimates were then used to arrive at installed plant costs. As Table 6.2 shows, approximately 2.6 million dollars is required to install the equipment associated with this control process.

Table 6.2. Capital Investment Requirements for Kidde Process Producing 29,000 TPY $(NH_4)_2SiF_6$ (1,000 TPD P_2O_5).

DIRECT COSTS	
EQUIPMENT, E	$ 652,000
PIPING	297,300
CONCRETE	33,250
STEEL	20,200
INSTRUMENTS	66,500
ELECTRICAL	13,000
INSULATION	32,000
PAINT	3,000
FIELD MATERIALS, M	465,250
DIRECT MATERIAL, E + M = M	1,114,250
DIRECT FIELD LABOR	410,000
SUB-TOTAL DIRECT COSTS	1,524,250
INDIRECT COSTS	
FREIGHT, INSURANCE AND TAXES	52,160
OTHER INDIRECTS (CONTRACTORS FEES, INTEREST DURING CONSTRUCTION, ENGINEERING)	565,300
SUB-TOTAL INDIRECT COSTS	617,460
CONTINGENCY (20% DIRECT AND INDIRECT COSTS)	428,342
TOTAL CAPITAL INVESTMENT (TCI)	$ 2,570,052

Table 6.3. Annualized Operating Costs for Kidde Process.

	Quantity	Unit Cost	Annual Cost
RAW MATERIALS			
SILICA	14,700 TPY	$ 35/TON	$ 514,500
AMMONIA	4,200 TPY	$190/TON	798,000
			$ 1,312,500
UTILITIES			
ELECTRICITY	350 HP	20 MILLS/KWH	$ 35,500
STEAM	37,500 LBS/HR	$0.50/M LBS	139,500
COOLING TOWER MAKE-UP	100 GPM	0.20/M GAL	8,930
			$ 183,930
OPERATING LABOR			
OPERATING	2 MEN/SHIFT	$ 5.50/HR	$ 102,300
SUPERVISION	15% OF OPERATING LABOR		15,345
			$ 117,645
MAINTENANCE			
LABOR AND MATERIALS (L&M)	4% OF TCI		$ 102,950
SUPPLIES	15% OF L & M		15,450
			$ 118,400
OVERHEAD			
PLANT	50% OPERATION & MAINTENANCE		$ 118,000
PAYROLL	20% OPERATING LABOR		23,530
			$ 141,530
FIXED COSTS			
DEPRECIATION (5% OF TCI)			$ 128,685
TAXES AND INSURANCE (2% OF TCI)			51,475
CAPITAL CHARGES (10% OF TCI)			257,370
			$ 437,530
TOTAL ANNUAL COSTS			$ 2,311,535
COSTS PER TON OF P_2O_5			$ 7.46

Annualized operating costs for the Kidde Process were obtained using estimates from Kidde's report and standard engineering estimates. A 310 day year was assumed to allow for equipment repairs and maintenance. Examination of Table 6.3 shows a net annual operating cost of $7.46 per ton P_2O_5. One will notice that no credit is given to the 29,000 TPY of $(NH_4)_2SiF_6$. This is explained by the fact that only one firm (Agrico Chemicals) in the U.S. produces this chemical. This firm indicated that they only market 2,000 TPY to commercial laundries where it is used to neutralize residual alkalinity between the wash and rinse cycles. Thus, even though this chemical has a current market value of $340 per ton, credit cannot be assigned since a market does not exist.

The question now arises concerning the feasibility of extending this process to include production of AlF_3. Although a detailed assessment was not made to determine the additional capital investment to do this (i.e., produce AlF_3), an estimate was made by pro-rating Kidde's data. This estimate indicates an additional investment of approximately $6.7 million to install a plant to process the $(NH_4)_2\ SiF_6$ to AlF_3. This plant would produce roughly 13,000 TPY of AlF_3, recycle NH_3 and SiO_2 to the fluorine recovery stages, and improve the economics of this control process significantly. A simplified flow diagram of this plant is included in Figure 6.3.

The above figures indicate that approximately 9.3 million dollars would be invested in a plant capable of servicing a 1,000 TPD P_2O_5 facility

Reproduced from
best available copy.

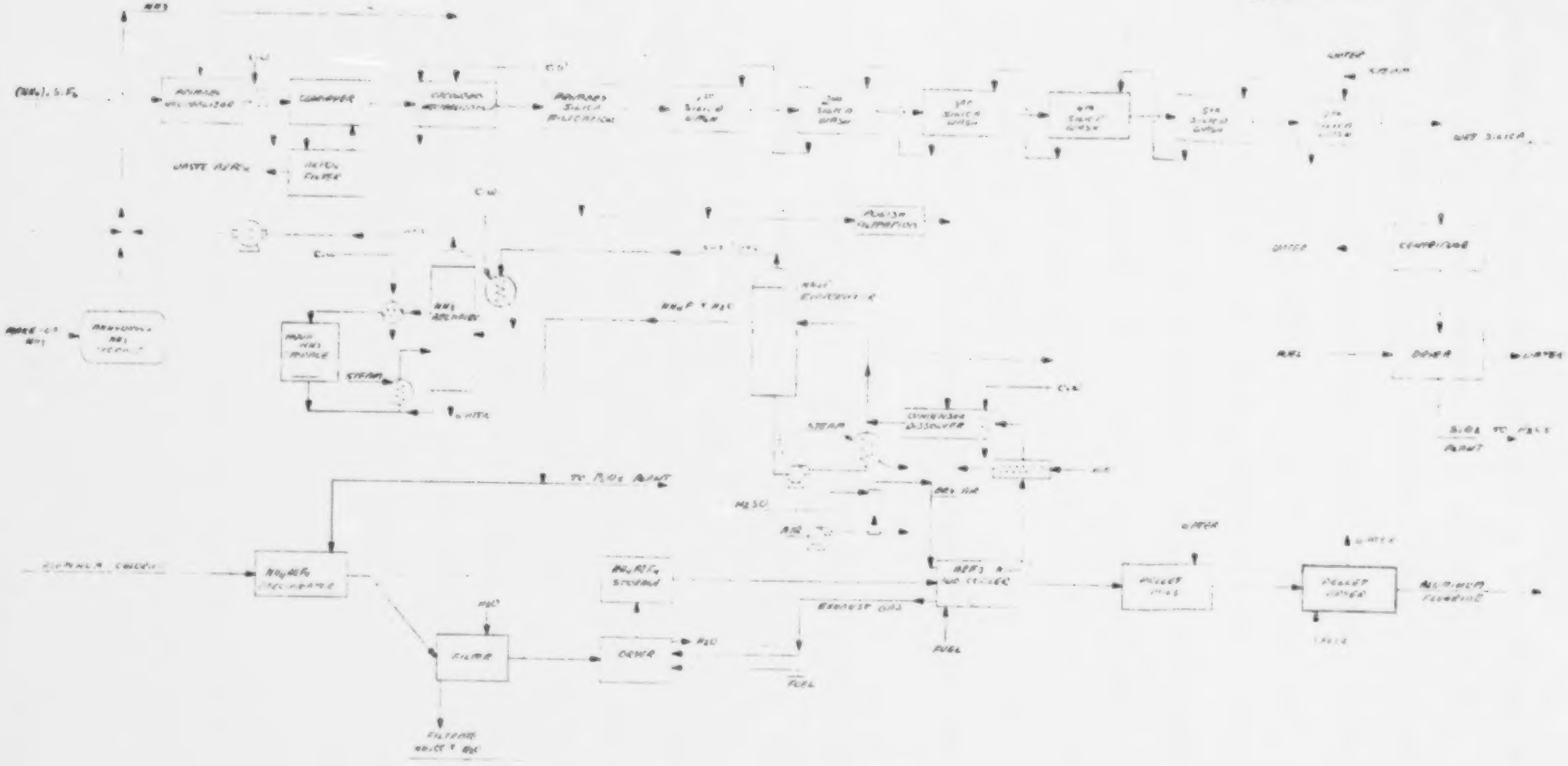


Figure 6.3. Kidde Process for Recovery of AlF_3 From Waste $(NH_4)_2SiF_6$.

(310,000 TPY). The present capital investment requirements for a 1,000 TPD P_2O_5 complex is approximately 15 million dollars. This is mid-1975 battery limits costs for an existing plant. Thus, the total investment required for the complete Kidde Process is of the same order of magnitude as that required for the P_2O_5 complex itself.

Although the current market for AlF_3 was not evaluated in this study, one aluminum manufacturer that was contacted (Kaiser) indicated that some market does exist for these chemicals used in producing aluminum. In fact, this company operates a small facility in the central Florida area where the sodium salt of fluosilicic acid is produced, shipped, and then used to make cryolite, a flux used in producing aluminum.

6.2 SWIFT PROCESS

The Swift Process was developed and patented by W. R. Parrish (patent No. 3273713), assignor to Swift and Co., Chicago, Ill. It involves the removal of fluorine compounds from wet phosphoric acid manufacturing in a manner similar to the Kidde Process.

6.2.1 Process Description

Figure 6.4 presents a process flow diagram as well as a fluorine and partial overall material balance for a wet process phosphoric acid plant producing 1,000 tons/day P_2O_5. Evaporation from dilute (28.5% P_2O_5) to concentrated (52.5% P_2O_5) is effected by three evaporation units in series. Vapors from each unit are scrubbed by an absorber which removes 90 percent of the fluorides evolved during each evaporation stage.

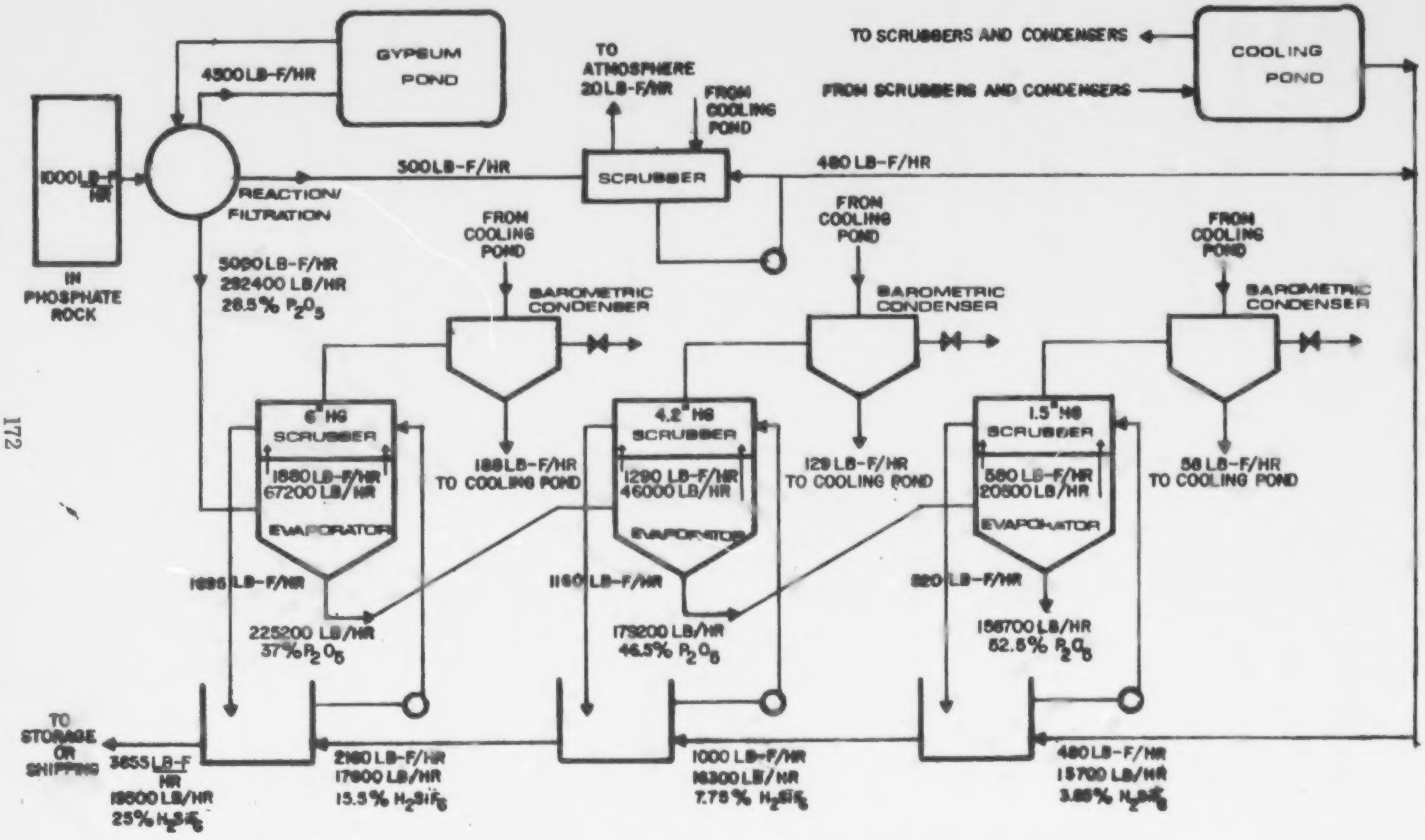


Figure 6.4 Swift Process for Fluorine Recovery at a 1000 TPD P_2O_5 Plant

A scrubber with a 96 percent fluoride removal efficiency is utilized for control of vapors gererated in the acidulation reactor. Cooling pond water is used as the absorbing medium and a stream of dilute (3.85%) H_2SiF_6 is continuously removed. This stream is introduced into a recirculation tank from which a solution of 7.75% H_2SiF_6 is drawn and pumped into the Swift vapor absorber servicing the third evaporator. The scrubbing liquor is introduced into the scrubbing unit through nozzles in the form of a spray. After absorbing the volatile fluorine material, the scrubbing liquor falls into a barometric leg, the end of which is immersed in the recirculation tank. The temperature of the liquor being recycled is maintained at a level which will ensure the absorption of volatile fluorine compounds while minimizing water vapor condensation at the operating pressure.

A solution of 7.75% H_2SiF_6 is drawn from the recirculation tank servicing the third unit and pumped into a recirculation tank servicing the second unit. The operational descriptions of the Swift components (absorber, recycle tank, and pump) servicing evaporation units 1 and 2 are identical to that described for evaporation unit 3. However, each unit is operated at a different temperature, pressure, and recycle rate, and a more concentrated stream of fluosilicic acid is drawn from each recycle tank. The product (25% H_2SiF_6) is continuously removed and transferred to storage tanks for shipment.

6.2.2 Process Applicability for Fluoride Emission Reduction

The original purpose of the Swift Process was for the economic recovery of byproduct fluorides and the realization of a return on investment. In the original report on gypsum pond emissions (November, 1974), the potential of the Swift Process as a means of controlling volatile fluorides emanating from these ponds was discussed. Since that date the original inventor, Parrish and his associate, Enriquez, have in fact recommended this process as a pollution control strategy when coupled with a two pond system. At least one phosphoric acid plant presented this process as its solution to potential fluoride emissions resulting from once-through river water for its process water requirements.

Table 6.4 indicates the level of fluoride recovery possible by the installation of the Swift Process. Of particular interest is the fact that fluorides entering the cooling pond are reduced by approximately 90 percent. Bearing in mind the fact that the gypsum pond is not effected and that it comprises only about 5 wet acres, it is the author's opinion that fluoride emissions should be reduced by 90 percent. The basis for this conclusion comes from the work of Tatera, who correlated fluoride concentrations in pond water with gaseous emissions.

6.2.3 Process Economics

A summary of capital costs is presented in Table 6.5. The primary pieces of equipment are three sets of recirculation tanks, pumps, and absorbers.

Table 6.4. Fluorine Material Balance in a 1,000 TPD P_2O_5 Plant Utilizing the Swift Vapor Absorption Process.

	With Swift	Without Swift
In Phosphate Rock	10,000 lb/hr	10,000 lb/hr
Recovered		
As 25% H_2SiF_6	3,855 lb/hr	0
Not Recovered		
Stays in gypsum	4,500 lb/hr	4,500 lb/hr
Lost at reactor	20 lb/hr	20 lb/hr
Stays in 52.5% P_2O_5	1,250 lb/hr	1,250 lb/hr
Lost to cooling pond	375 lb/hr	4,230 lb/hr

Table 6.5. Capital Investment Requirements for the Swift Vapor Absorption System.

Capital Investment (Installed Costs)	
1. 2 Scrubbers handling 140,000 ft^3/min each @ $282,000 each	$ 564,000
2. 1 Scrubber handling 180,000 ft^3/min	362,000
3. 3 Rubber-lined recirculation tanks handling 1,050 gal each @ $29,100 each	87,300
4. 3 Stainless steel recirculation pumps (900 gpm @ 100 psi) $40,900 each	122,700
5. 4 Rubber-lined storage tanks 100,000 gal capacity @ $42,000 each	168,000
TOTAL CAPITAL INVESTMENT	$ 1,304,000

The rest of the equipment shown in Figure 6.4 is required even without the Swift Process. Storage facilities consisting of four rubber-lined tanks are required to hold one week's supply of 25% H_2SiF_6 produced.

Costs will vary greatly depending upon whether the plant is existing or new. These costs were derived for retrofit to an existing plant. The figures presented compare well with those quoted by a manufacturer of \$500,000 for the equipment servicing each evaporator of \$1,500,000 total capital investment for three modules.

Annualized operating costs are presented in Table 6.6. Assuming no income from the sale of fluosilicic acid, the increase in price of one ton of P_2O_5 would be \$1.25. At the present market value of \$60/ton H_2SiF_6*, the Swift Vapor Absorption Process will operate at a profit of \$2.26/ton of P_2O_5 if all fluosilicic acid produced is sold. It was this potential profit which prompted several firms to utilize the Swift Process on the basis of economics. As previously stated, a marketing survey was not conducted. However, it is doubtful that all plants in the U.S. could utilize the process and realize a profit on their venture. Its use would have to be accompanied by a vigorous marketing effort and possible price reduction in order to make by-product fluosilicic acid a more attractive source of fluorides than Mexican fluorspar.

If gypsum and cooling pond are high emitters of fluorides and control equipment is required, the Swift Process is an attractive low cost or low profit abatement system.

---

*FOB Plant

Table 6.6. Annualized Operating Costs for Swift Process.

	Quantity	Unit Cost	Annual Cost
UTILITIES			
ELECTRICITY	250 hp	20 mills/KWH	$ 27,730
OPERATING LABOR			
OPERATING	1/2 MAN/SHIFT	$ 5.50/HR	$ 24,000
SUPERVISION	15% OF OPERATING		3,600
			$ 27,600
MAINTENANCE			
LABOR AND MATERIAL	4% OF CAPITAL INVESTMENT		$ 52,160
SUPPLIES	15% OF LABOR AND MATERIAL		7,840
			$ 60,000
OVERHEAD			
PLANT	50% OPERATION & MAINTENANCE		$ 43,800
PAYROLL	20% OPERATING LABOR		5,520
			$ 49,320
FIXED COSTS			
DEPRECIATION (5% OF CAPITAL INVESTMENT)			$ 65,200
TAXES AND INSURANCE (2% OF CAPITAL)			26,080
CAPITAL CHARGES (10% OF CAPITAL)			130,400
			$ 221,680
TOTAL ANNUAL COST			$ 386,330
COST PER TON OF P_2O_5			$ 1.25
CREDIT			
18,114 TONS 100% H_2SiF_6 @ $ 60/TON			$1,086,870
ADJUSTED ANNUAL CREDIT			$ 700,530
CREDIT PER TON P_2O_5			$2.26

6.3 LIMING OF COOLING PONDS

Treatment of effluents by "double-liming", or two-stage lime neutralization, has been practiced by wet-process phosphoric acid plants for many years. The process simultaneously raises the pH while lowering the concentration of soluble fluorides.

6.3.1 Process Description

Under the assumption that a two pond system will be used to segregate gypsum sluicing water from other process water, cooling pond water will contain fluorides and small amounts of P_2O_5. Thus it is necessary only to add sufficient lime to precipitate out fluoride compounds as fluorspar (CaF_2). Most fluorides from the scrubbers and barometric condensers will be in the form of fluosilicic acid. Upon addition of sufficient lime, fluorides will be precipitated according to:

$$H_2SiF_{6(aq)} + 3CaO_{(s)} + H_2O \qquad 3CaF_{2(s)} + 2H_2O + SiO_{2(s)} \tag{6.8}$$

Holding the mixture in a quiescent area allows the particulate CaF_2 to settle.

Table 6.7 shows the reported effect that liming has on actual cooling pond water. As this Table shows, a pH of 3.9, soluble fluorides are only one percent of the value at a pH of 1.4. Figure 6.5 shows a graph of fluoride vapor pressure versus pH from the data in Table 6.7. Use of this figure allows one to calculate the potential emissions reductions to be expected by liming the pond waters. Thus, at a pH of 3.9, the

Table 6.7. Effect of Liming on Fluoride Evolution From Gypsum-Pond Water

pH	Soluble fluoride, ppm	$Ca(OH)_2$, lb/gallon	Vapor pressure of fluoride @25°C, mmHg
1.4	8125		13.8×10^{-6}
2.6	4000	0.116	6.22×10^{-6}
3.0	NR	0.145	NR
3.3	450	0.156	NR
3.9	106	0.157	NR
4.5	100	0.160	0.86×10^{-6}
6.1	106	0.192	0.45×10^{-6}
6.25	NR	0.193	NR
7.72	NR	0.207	NR
9.7	NR	0.213	NR
12.1	NR	0.222	NR
12.3	NR	0.246	NR
12.5	16	0.346	NR

SOURCE: (HEW, 1970)

NR: Not Reported

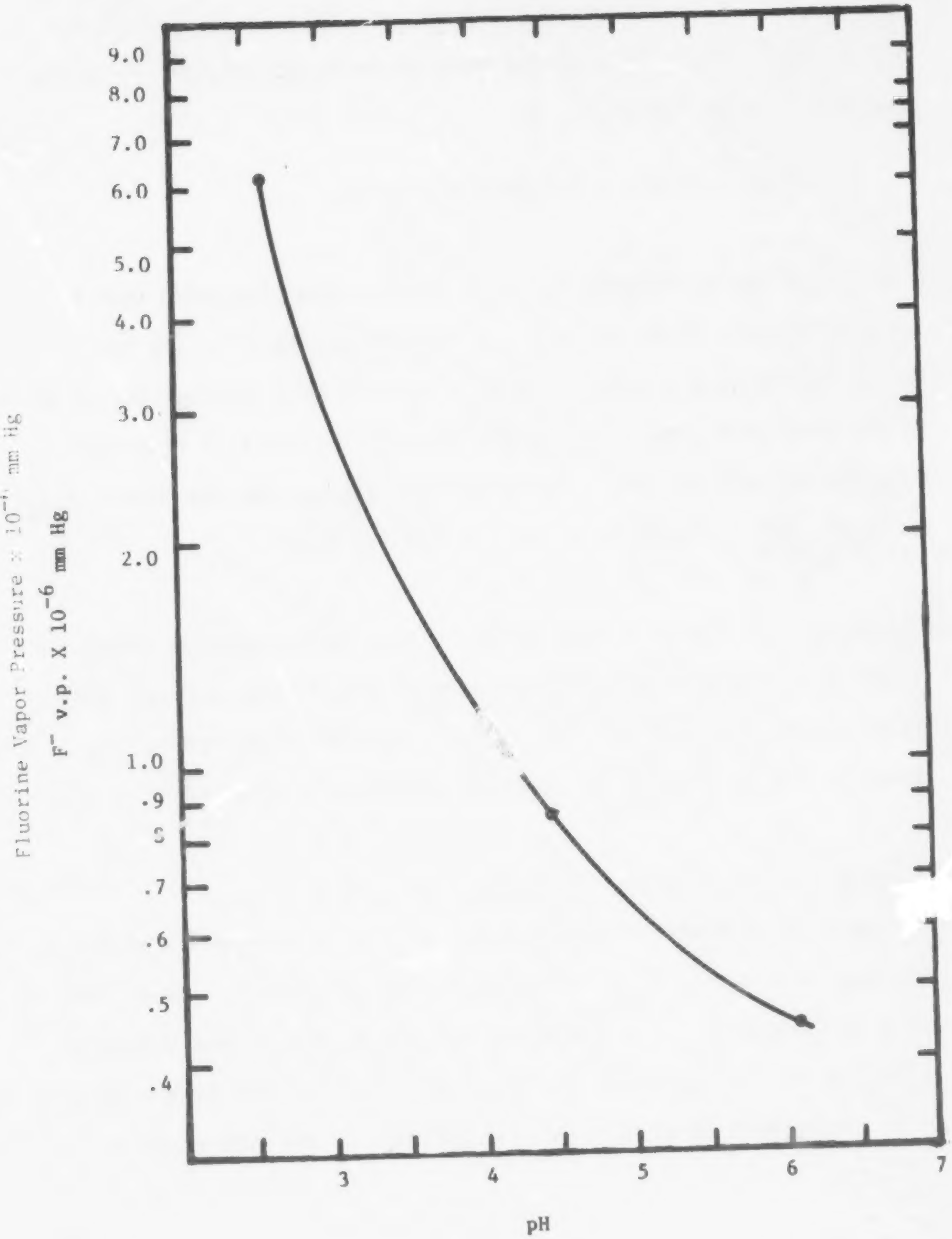


Figure 6.5. **Fluoride Vapor Pressure vs. pH** (Source: HEW, 1971)

fluoride vapor pressure obtained through interpolation of this figure is 1.3×10^{-6} mmHg. The expected emission reduction obtained in liming from pH 1.4 to pH 3.9 is:

$$\text{Reduction} = (13.8 - 1.3)100\%/13.8 = 90.6\%$$

A pH of 3.9 can be achieved by single stage liming. Assuming that a two pond system will be employed, it will be necessary to lime the entire cooling pond contents from pH 1.4 to 3.9 only once and thereafter to add sufficient lime to handle the theoretical amount of fluorides entering the cooling pond. Thereafter the major acidic components, P_2O_5 and H_2SO_4, are confined to the gypsum sluicing water.

Figure 6.6 is a schematic diagram of a modern well-controlled single stage liming system. Although not shown in this figure, a rotary kiln for calcining limestone and the auxillary equipment required for its operation are included in the proposed scheme and cost estimates.

6.3.2 Fluoride Emission Reduction by Single Stage Liming

The reduction of fluoride emissions by liming is a consequence of the reduction of fluoride vapor pressure upon the addition of lime as indicated in Table 6.7. It is estimated that for a cooling pond having an initial pH of 1.4, emissions can be reduced by 90 percent by the addition of 0.157 pounds $Ca(OH)_2$/gallon to the contents of the pond (Table 6.7).

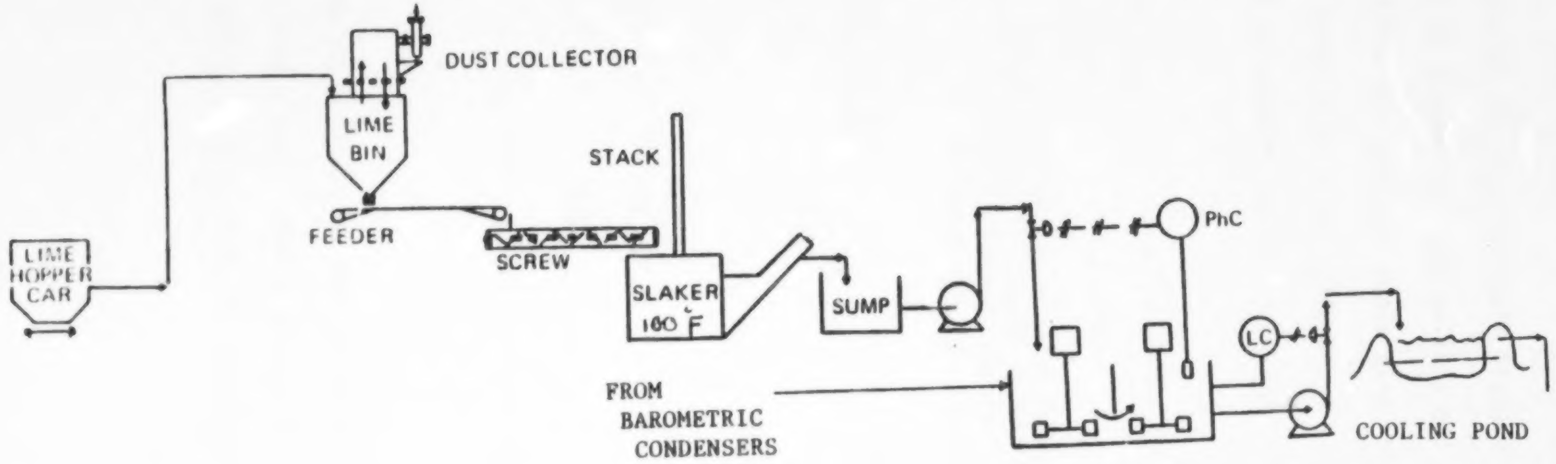


Figure 6.6. Proposed Single Liming System

Table 6.8 presents an overall fluoride material balance. The quantity of fluorides entering the cooling pond is reduced by 90 percent. Since the gypsum pond occupies only about 5 acres, and since fluorides present in the gypsum are mostly solid CaF_2, it is this study's estimate that overall gaseous fluoride emissions can be reduced by 90 percent by liming to a pH of 3.9 to 4.0.

Table 6.8

Fluorine Material Balance in a
1,000 TPD P_2O_5 Plant Utilizing Liming
as Fluoride Control Strategy
Basis: 10,000 lbs/hr F

Item	With Liming	Without Liming
Gypsum cake	4,500	4,500
Precipitated by liming	3,807	
Vapors from reactor	20	20
52.5% P_2O_5	1,250	1,250
Cooling pond	423	4,230

6.3.3 Process Considerations

Installation of single-liming systems at existing phosphoric acid plants should pose few, if any, problems. Most plants already have double-liming treatment systems for pond water overflow discharge.

This study proposes use of a single-liming facility as shown in Figure 6.6. Lime requirements for a 1,000 TPS P_2O_5 plant are arrived at as follows.

First, an initial, one-time dose of lime is required to bring the existing cooling pond water up to the required pH of 3.9 to affect a 90 percent emissions reduction. Acidic constituents of the existing pond requiring neutralization at this point are P_2O_5, H_2SO_4, and H_2SiF_6. The initial lime requirements are calculated based on the following assumptions, applicable to a 1,000 TPD plant:

1. 300 acres of cooling pond waters at an average depth of 0.5 meters (160 MM-Gal).
2. 0.157 lbs $Ca(OH)_2$ is required to treat each gallon (see Table 6.7)

Based on these assumptions, 9,530 tons of lime (as CaO) are initially required to raise the pH to 3.9. Before this lime is added, the gypsum and cooling ponds are segregated to ensure the integrity of the proposed system.

The second phase of the liming program occurs once steady-state has been achieved after the initial dosage has been applied. The quantities of lime required during steady-state are determined from equation 6.8. The lime requirements according to this equation are 1.47 lbs CaO per lb fluorine (3 moles CaO/6 moles F). Based on data presented in Section 2.2 of this report, we estimate that approximately 91 lbs F/ton P_2O_5 will end up in the cooling pond waters. This includes fluorine scrubbed from the reactor vapors and that removed in the barometric condensers. Based on these data and assumptions, 135 lbs CaO per ton P_2O_5 will be required during steady-state operation (67.3 tons per day).

During the initial dosage two quantities of lime will be required--that necessary to raise the pH and the daily steady-state requirements. If we now assume a 40-day transient period to achieve steady-state, the initial daily requirement will be 305 tons CaO/day (9530/40 + 67.3).

6.3.4 Process Economics

A summary of capital costs associated with liming is presented in Table 6.9. For the large quantities of lime required, it will be more economical for the plant to produce its own lime from limestone. Thus, included in the capital costs are a kiln, limestone bins, and a scrubber for the control of particulate emissions from the kiln. The other major expenses are the chemical feed system as well as the initial lime requirement which have been included into the total capital investment.

Annualized operating costs are presented in Table 6.10. The greatest costs are those associated with fuel to calcine the limestone. Depreciation and capital charges comprise approximately 33 percent of annualized costs. Total annualized costs using this strategy will result in an estimated cost increase of \$3.13/ton P_2O_5.

Table 6.9. Capital Investment Requirements for Single Liming System.

Capital Investment (Installed Costs)	
1. Lime kiln (8' x 140" with motor)	$ 1,100,000
2. Lime kiln scrubber (includes fan, motor, ducting)	61,000
3. Limestone bins and conveyors	120,000
4. Chemical feed system (including slaker, pump, storage, reaction vessel)	283,000
5. Miscellaneous (20% of equipment costs)	95,400
6. Initial lime requirements (9,530 tons @ $47/ton)	447,910
TOTAL CAPITAL INVESTMENT	$ 2,107,310

Table 6.10. Annualized Operating Costs for Single Liming.

	Quantity	Unit Cost	Annual Cost
RAW MATERIALS			
LIMESTONE	120 TPD	\$ 4/TON	\$ 149,000
UTILITIES			
ELECTRICTY	50 hp	20 mills/KWH	\$ 5,070
FUEL	3.1 mm-BTU/Ton $CaCO_3$	\$2/mm-BTU	230,600
			\$ 235,670
OPERATING LABOR			
OPERATING	1 MAN/SHIFT	\$ 5.50/HR	\$ 48,200
SUPERVISION	15% OPERATING		7,200
			\$ 55,400
MAINTENANCE			
LABOR AND MATERIAL (L&M)	4% OF TCI		\$ 81,624
SUPPLIES	15% OF L & M		11,884
			\$ 93,508
OVERHEAD			
PLANT	50% LABOR & MAINTENANCE		\$ 74,454
PAYROLL	20% OPERATING LABOR		11,080
			85,534
FIXED COSTS			
DEPRECIATION (5% OF TCI)			\$ 102,030
TAXES AND INSURANCE (2% OF TCI)			40,812
CAPITAL CHARGES (10% OF TCI)			204,060
			\$ 346,902
TOTAL ANNUAL COST			\$ 971,084
ANNUAL LIMING COST			
\$/TON CaO			\$ 46.62
\$/TON P_2O_5			\$ 3.13

6.4 GYPSUM TRANSPORT BY CONVEYOR BELT

Transporting the gypsum by-product to storage piles using dry conveyor belt rather than slurry pipeline could possibly reduce the fluoride emission from this segment of P_2O_5 production. The benefits (i.e., emissions reductions) are not as apparent as the annual costs are calculable. This is because the gypsum filter cake contains some phosphoric acid and between 18-35 percent free moisture. Thus the pH of this water will most likely be low and the fluoride vapor pressure high. If it were possible to keep these solids dry once the free water evaporated, the emissions would be negligible due to the very small vapor pressure of most solids at ambient temperatures. However, operation of a gypsum stack does not readily accomodate covering the stack to reduce emissions either with dirt or some other impervious barrier.

Although several plants in Belgium are reported to be using a belt conveyor, the authors have knowledge of only one dry-belt system in the U.S., in California. Apparently it is economically justified in those cases where the gypsum can be marketed for agricultural and other uses.

Capital investment requirements for a one-mile by 24-inch covered conveyor are presented in Table 6.11. These costs were estimated assuming 4.5 tons gypsum per ton of P_2O_5 with 25 percent free moisture included (Slack, 1968). A six year life was assumed based on vendor estimates of a useful life of 8 to 10 million tons transported.

Table 6.11. Capital Investment Requirements for Dry Gypsum Conveyor.

Capital Costs	
Belt conveyor--one mile @ $200/ft	$ 1,056,000
Feeders including motors (2 each)	10,000
TOTAL CAPITAL INVESTMENT	$ 1,066,000
Annualized Operating Costs	
Depreciation ($\frac{100}{6}$ = 16.7%)	$ 178,000
Capital charges (10%)	106,600
Operating costs @ $ 0.08/ton-mile (vendor estimate)	148,800
TOTAL ANNUALIZED COSTS	$ 433,400
$/TON P_2O_5 PRODUCED	$ 1.40

Annualized operating costs, also presented in Table 6.11, of approximately \$1.40 per ton of P_2O_5 were estimated. Although other measures would most likely need incorporation for this system to be effective, the additional costs were not estimated. These measures might include some form of covering material on the dry gypsum stack and water treatment facilities for surface runoff and seepage.

Although approximately 45 percent of the original fluorine in the rock is retained in the gypsum, the potential emissions from this source are most likely the smallest when the gypsum and cooling ponds are separated. This should be true even with commonly used slurry transport techniques due to the small area requirements for the gypsum piles.

6.5 PRETREATMENT OF ORE BY CALCINING

6.5.1 Process Description

Precalcining the phosphate rock prior to accidulation with sulfuric acid was considered as one candidate control process. Calcination involves heating the rock in a rotary kiln or fluid bed reactor. Although direct and indirect firing may be used, the latter method has some disadvantages as discussed below. As currently practiced in producing animal feeds, the rock is calcined by direct firing methods.

Defluorination of phosphate rock occurs in two regimes. In the first, low-temperature regime, up to 66 percent of the fluorine can be removed by heating the rock to approximately 2,000°F. Heating the rock to its fusion temperature, which ranges from 2,500°F to 2,700°F volatizes another 21 to 24 percent which increases the fluorine removal to approximately 90 percent. The prevalent gaseous species involved is HF, although SiF_4 is present in smaller amounts, with the ratio $HF:SiF_4$ increasing with increasing temperature.

The off-gases from this reaction must be cooled and scrubbed to remove particulates and fluorides before the gases are vented to the atmosphere. Herein lies one of the chief disadvantages to this approach. First, the gas volumes handled with direct firing are large (approximately 500 ACFM/ton P_2O_5 at 2,000°F) and second, the fluorides scrubbed from the gases must be disposed of, generally in the scrubber water cooling pond. As currently practiced, cooling pond water is used to scrub the gases and is neutralized before returning to the cooling pond. Thus, indirect-firing only removes the fluorine from the rock to have it placed in the pond.

Indirect-firing in a rotary kiln reduces the quantity of off-gases that must be handled. However, the temperatures that are obtained by this method are limited to 1,200°F for stainless steels; use of special metals will increase this to 2,000°F, but at a great additional expense.

As proposed herein, two direct-fired rotary kilns will treat 3,000 TPD of phosphate rock. Prior to scrubbing, the hot (ca. 2,000°F) off-gases will be cooled to 500°F by waste heat boilers which will produce approximately 300,000 lbs/hr low pressure (150 psi) steam. This last provision will improve the economics somewhat by providing a steam credit.

6.5.2 Process Economics

Capital investment and annualized operating costs are presented in Table 6.12. As this Table shows, the capital required to install kilns to treat 3,000 TPD of rock is roughly $30 million, nearly twice the investment of the P_2O_5 plant itself. This is without any fluorine byproduct recovery. Since scrubbing the gases only produces a one to two percent solution of H_2SiF_6, additional equipment would be needed to concentrate this to the 25 percent, which is the normal saleable concentration.

6.6 HEMI/DIHYDRATE PROCESS

The hemihydrate-dihydrate process for making wet-process phosphoric acid has been in use in Japan for several years. Its primary advantages are the higher overall yield of P_2O_5 and the production of high quality gypsum, suitable for gypsum plaster and gypsum boards. About 40 percent of fluorides present in the rock are volatilized in the acidiculation stages and may be recovered as fluosilicic acid.

6.6.1 Process Description

Although there are several variations of this process, they basically differ from the common dihydrate process in that hemihydrate is formed during decomposition of the phosphate rock and is subsequently recrystallized as dihydrate before filtration. The decomposition and recrystallization steps are carried out in separate reaction vessels to allow optimum process control. The resulting dihydrate crystals, as compared with those made in the common dihydrate process, are larger and retain less P_2O_5 and other impurities in the lattice.

Table 6.12. Capital Investment Requirements for Pre-Calcining of Phosphate Ores.

Capital Costs	
Rotary kilns: 2 - 16.5' x 600' direct fired (installed costs, mid-1975)	$ 28,400,000
Waste-heat boiler (2)	700,000
Gas-scrubbers (2)	710,000
TOTAL CAPITAL INVESTMENT	$ 29,810,000
Annualized Operating Costs	
Fuel	$ 1,060,000
Electricity (1,400 hp @ $ 0.20/KWH)	175,000
Depreciation (10% TCI)	2,981,000
Maintenance (5% TCI)	1,490,500
Capital Charges (10% TCI)	2,981,000
TOTAL ANNUALIZED COSTS	$ 8,687,500
Steam credit (300,000 lbs/hr @ $ 0.50/M-1b)	1,116,000
NET ANNUAL OPERATING COSTS	$ 7,571,500
$/TON P_2O_5 PRODUCED	$ 24.42

The key to the process is growing large, easily filterable crystals at a rate fast enough to give economic operation, reducing the phosphate substitution in the process. The diyhydrate is thus crystallized under quiescent, carefully controlled conditions, thereby making it possible to maintain a uniform excess of sulfuric acid throughout the slurry.

6.6.2 Effect of Hemi/Dihydrate Process on Fluoride Emissions

There is virtually no data available to allow a judgment to be made on any fluoride emissions reduction which would result from employing the Hemi/Dihydrate process.

In order to make an estimate of potential fluoride emissions reductions, the following will be assumed:

1. 45 percent of the fluorides initially present in the rock will remain in the by-product gypsum.
2. 12 1/2 percent of the fluorides will be present in the product acid.
3. 0.2 percent of the fluorides will be released to the atmosphere.
4. 42.3 percent (or the remainder) of the fluorides will either be recovered or end up in the cooling pond.
5. 30 to 40 percent of the fluorides are recoverable as fluosilicic acid (as claimed by the manufacturer).

Based on the above, it is estimated that 70 to 95 percent of the fluorides which could contribute to cooling pond emissions can be recovered as by-product H_2SiF_6.

The common dihydrate process is based on a rather violent reaction which produces local deficiencies of sulfuric acid, and thus leaves P_2O_5 in the dihydrate lattice. As a result of the better control in the hemihydrate-dihydrate process, loss of phosphate by lattice substitution is very low. Recovery is thus improved and the by-product gypsum is more suitable for use in building products.

Figure 6.7 presents a flow diagram of the Fisons Ltd. scheme for wet process phosphoric acid manufacture. The notable differences with this scheme from those employing dihydrate routes are that:

1. No evaporators are utilized since a 50 percent P_2O_5 product is obtained in the reactors.
2. A much higher amount, which is estimated to be 30 to 40 percent of all fluorides initially present in the rock, is evolved in the reaction/filtration step. These vapors are sufficiently rich in fluorides to allow the production of fluosilicic acid as a saleable by-product.

6.6.3 Process Economics

Since the hemihydrate-dihydrate process is an alternative to the existing U.S. wet phosphoric acid processes, the economics cannot be evaluated in the same manner as the previous "add-on" control systems. In order to use the hemihydrate-dihydrate process, the existing plant must be extensively changed and markets found for the gypsum and fluosilicic acid produced. The success of the process in Japan rests largely on the facts that Japan must import all phosphate rock and most of its gypsum. Thus

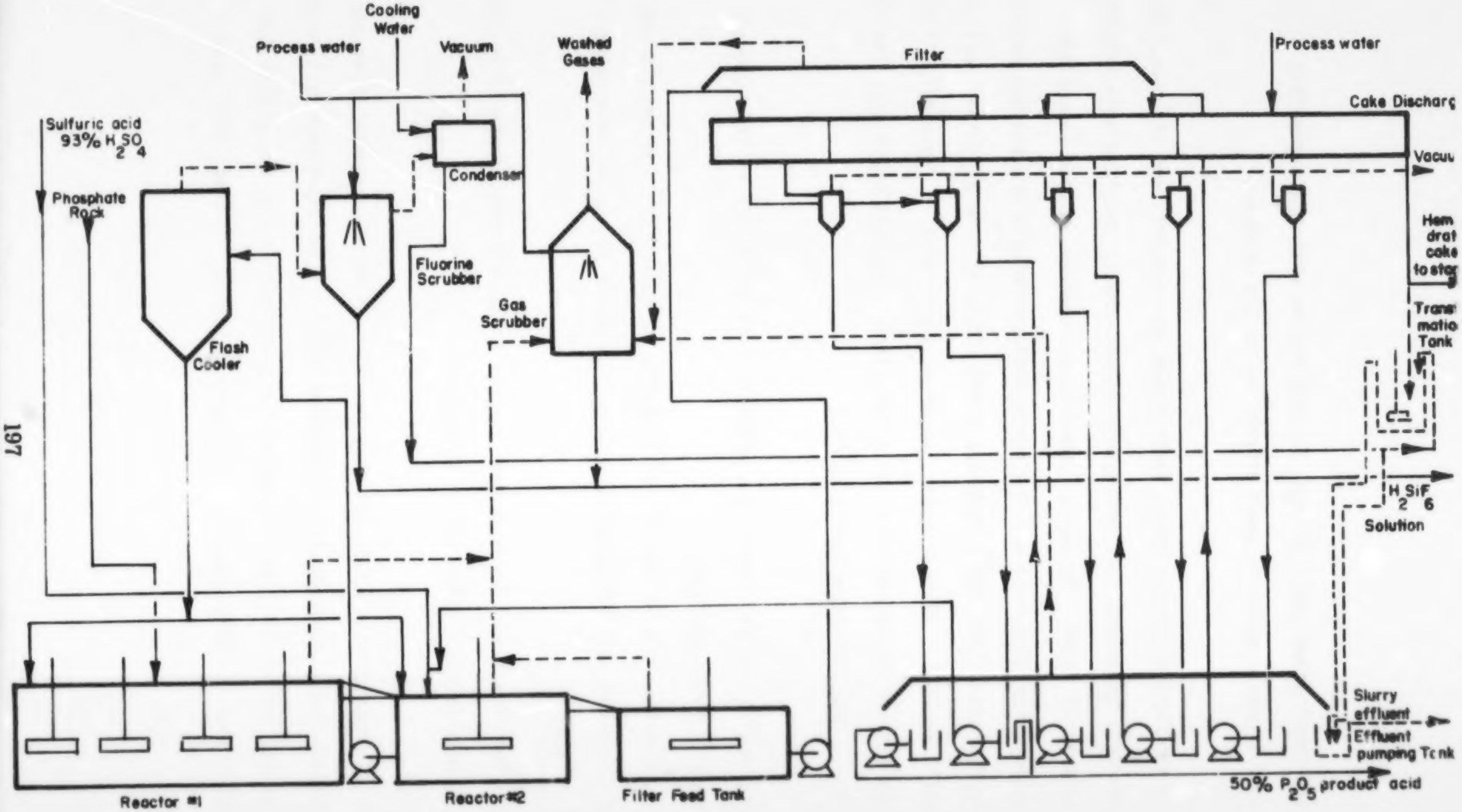


Figure 6.7. Hemi/Dihydrate Wet Process for Phosphoric Acid Manufacture. Fisons Ltd. Scheme.

the small added yield of P_2O_5 in combination with the production of a useful gypsum makes it most attractive to the Japanese.

In the United States, these factors are not present, and the relatively low cost phosphate rock and gypsum do not create the favorable economics here as in Japan. By way of comparison, however, a cost comparison between the dihydrate and the hemihydrate-dihydrate process was developed by Fisons Ltd. for a European plant using Morocco phosphate rock and built in 1971. This analysis, which is summarized in Table 6.13, indicates the process is competitive for a new plant. Capital costs are also included for a 1,000 TPD plant built in 1975.

The Hemi/Dihydrate routes are presently not practiced in this country. Reasons given include:

1. Florida rock is not of sufficiently high quality to allow its use.
2. Problems are encountered in the filtration operation when using Florida rock.
3. The relatively large amount of clay fines and other impurities make this process difficult to control.

It is important to point out that, in fact, several Japanese firms use Florida rock successfully. Sometimes calcining is practiced to improve the quality of the rock. However, it is foreign firms which have the experience in Hemi/Dihydrate acid production and no doubt hold many

Table 6.13. Comparative Process Economics*

(Basis: European plant (built in 1971) using Morocco rock to make 50,000 metric tons of P_2O_5/year as 50% phosphoric acid)

	Typical Dihydrate Process		Hemihydrate Process		Two-state Hemi/Dihydrate Process	
Extraction efficiency, % (based on measured cake losses)	96.3		94.0		98.5	
Operating costs/ton P_2O_5	Quantity	Cost, $	Quantity	Cost, $	Quantity	Cost, $
Phosphate rock, tons	3.10	56.83	3.17	58.12	3.03	55.54
Sulfuric acid (100%), tons	2.73	50.05	2.77	50.78	2.70	49.49
Low-pressure stream, tons	2.00	5.67	0.20	0.57	--	--
Fresh water, tons	7.00	0.84	6.00	0.72	7.00	0.84
Cooling water, tons	37.50	0.50	22.00	0.27	22.00	0.27
Electricity, kwh	115.00	1.92	125.00	2.08	135.00	2.25
CAPITAL COSTS, $		3,333,000 (12,917,000)**		2,333,000 (9,041,000)**		2,695,000 (10,444,000)**
Depreciation, interest, taxes and insurance (20%)		667,000		467,000		539,000
Maintenance (7%)		233,000		163,000		189,000
Operating labor, men/shift	3	73,500	2	55,500	3	73,500
OVERALL PRODUCTION COST, $/METRIC TON P_2O_5		135.28		126.25		124.42

* Battery limits costs for phosphoric acid plant only, excluding rock, sulfuric acid and product acid storage. Additional expenses such as supervisory labor, overheads, charges on working capital, which are common to the three processes, are not included. No allowance has been made for the cost of fluorine recovery, or for the use of defoaming agents that may be required for certain rock types, but rock grinding and clarification costs for the dihydrate process have been included.

**Adjusted for 1,000 TPD plant built in July, 1975.

patents and rights associated with these schemes. It is therefore very difficult at the present time to calculate cost comparisons for such plants when built by American firms in the United States.

7.0 DEMONSTRATION COSTS

In this section demonstration costs for two items are considered. First, a methodology for determining fluoride emissions from gypsum ponds is discussed; costs for the proposed method are then presented. In the second portion of this section demonstration costs are presented for determining the effectiveness of the control method selected by this study as the most cost-effective candidate.

In summary, the costs for these items are:

Field verification of emission rate (2 ponds)	$ 70,925
Demonstration of Swift system (1 pond)	
a) pilot plant	$295,760
b) modification of existing plant	$274,475

As pointed out in section 7.2.2, the last item listed could be in error by approximately $25,000. This is due primarily to the uncertainties in estimating costs for pond segregation without site-specific data.

7.1 VERIFICATION OF PREDICTED FLUORIDE EMISSIONS

Based on our findings concerning the emissions of fluoride from gypsum ponds, it was concluded that no investigator had as yet established experimentally the fluoride emission rate from gypsum ponds. While King has conducted experiments in which ambient fluoride concentrations were measured, he did not directly measure the emission rate. Even though his predicted concentrations correlated quite well with his measured values, the mathematical dispersion model used in his predictions is not exact and, as pointed out in Section 5.0 of this report, might tend to overestimate.

For the above reasons, the following experimental program is proposed which would 1) directly measure fluoride emissions as a function of velocity and 2) verify the ambient ground-level fluoride concentrations predicted in section 4.3 of this report.

Fluoride emissions would be measured as follows. All fluorides emitted from the pond must pass through an imaginary vertical plane passing through the downwind dike of a gypsum cooling pond and extending the length of the pond. If, at any height z_i above the dike, the fluoride concentration and wind velocity are known, the mass flux at that point can be determined. Mathematically stated:

$$E = VW\Delta ZC$$

where: W = width of pond

ΔZ = difference in height

C = fluoride concentration

By determining the flux at several heights above the dike, the total mass of fluorides passing through the plane is:

$$E_T = \sum_{i=1}^{i=N} V_i W \Delta Z_i C_i \qquad (7.1)$$

where: $C_N \doteq 0$

One possible method for measuring concentrations at various heights would be to construct towers at each end of the gypsum pond. A remote long path infrared sensor could then establish the average concentration over the total length of the pond at different heights. The concentration profile obtained from this operation could then be used, together with the velocity profile, to calculate the fluoride emission rate.

The above approach presents some practical problems that might be hard to overcome. The biggest problem would be alignment of the remote IR source with the detector. As the system got progressively higher up the towers, the wind would most likely make it difficult, if not impossible, to keep the units aligned.

One advantage to the above approach is that by using a dispersive infrared detector, one could determine which fluoride compounds were being emitted.

Another approach that could be taken to determine the emissions is to install ambient fluoride samplers at different heights on the towers. However, it is suggested that the towers now be located at points equidistant from the ends of the pond (1/3L and 2/3L).

Figure 7.1 shows a theoretical concentration profile predicted by the finite line source dispersion model discussed in Section 5.3 of this report. As the curves in this figure indicate, the ambient concentration 30 meters above ground level should be about ten and twenty-five percent of ground-level concentrations for stability class four

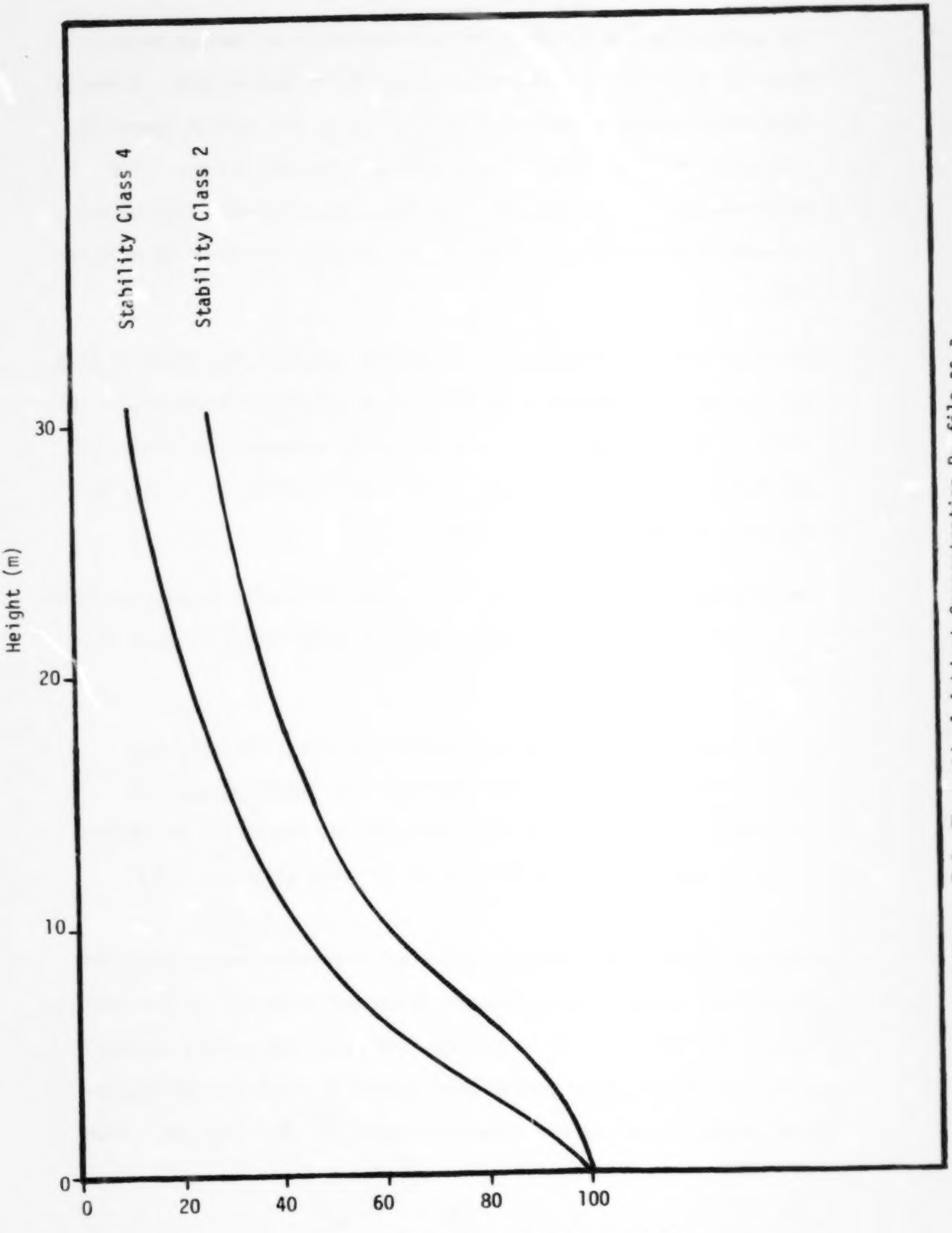


Figure 7.1 Theoretical Ambient Concentration Profile as a Vunction of Height

and two respectively. Thus, a 100 foot tower with five ambient samplers equally spaced should be sufficient to establish the concentration profile.

Velocity profiles can be established with three cup-anemometers placed at different heights, e.g., 2, 8 and 16 meters. Recorded wind speeds can be used to establish the value of the power low exponent in equation 4.38 for each experiment conducted.

Once the concentration and velocity profiles are determined, the emission rate is calculated through equation 7.2.

To further verify King's and Tatera's equations for fluoride emission rates, the following data should be collected for each experiment. Ten centimeter wind velocity (Tatera), average temperature for the pond water in each line source (Tatera and King), average liquid fluoride concentration in each line source (vapor pressure) and ambient temperature and cloud cover (for stability).

To establish the accuracy of the ambient fluoride concentrations predicted in Section 5.0 of this report, a network of ambient samplers should be placed downwind of the pond, e.g.,at 100, 200 and 300 meters. One sampler should also be placed upwind to establish the background fluoride concentration.

7.1.1 Sampling Methods

It is important that an appropriate sampling method be used that will ensure results that are as accurate as the state-of-the-art permits.

For several years the State of Florida Department of Pollution Control has been monitoring ambient fluoride levels in the vicinity of the phosphate mining and processing area near Lakeland, Florida. The sampling method used by this agency consists of a series of midget impingers containing either sodium hydroxide or distilled water. This method is under question, however, as one investigator (Sholtes, 1973) found that in the concentration range of 10-100 ppm gaseous fluorides, the collection efficiency decreased in direct proportion to the gas concentration. Collection efficiencies as low as 30 percent were measured in this range.

The ambient sampler used and evaluated by King was also tested by the EPA (Baumgardner, CPL). This sampler consisted of a 15 foot length of 6MM I.D. coiled glass tube coated with Na_2CO_3. Ambient air is drawn through this tube at approximately 30 LPM for one hour at which time the glass tube is flushed with a buffer solution. The fluoride content of the buffered Na_2CO_3 solution can then be determined with a specific ion electrode.

Evaluation of a commercial model of the above sampler by the EPA indicated unusually large response times when the unit was calibrated using an 8 foot length of small bore teflon tubing placed upstream of the glass tubing. King reported a collection efficiency of 85 percent for a 15 foot length of glass tubing and 95 percent for two 15 foot lengths connected in series which should be sufficient for the purposes of the experiments proposed herein.

7.1.2 Experimental Design

In order to gather sufficient data to verify the fluoride emission estimates of King and of Tatera, it is proposed that two ponds be tested, preferably at two different plants. Ponds of roughly rectangular shape should be utilized in order to minimize the number of assumptions made in determining the fluoride flux.

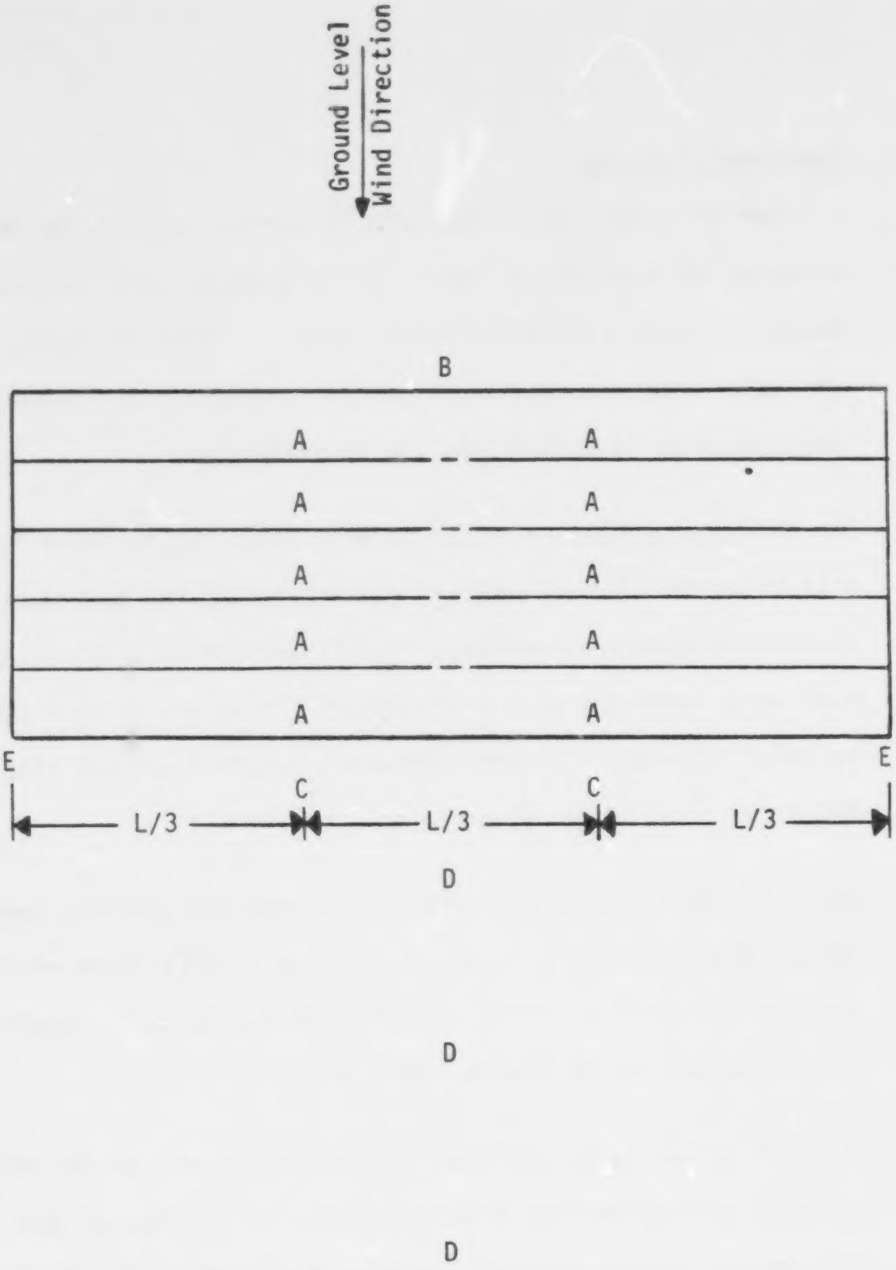
Two telescoping meteorological towers, installed as shown in Figure 7.2 will house the ambient samplers and meteorological equipment. Prior to performing each experiment, it will be necessary to measure the pond water temperature at a minimum of two points in each line source, as shown in Figure 7.2. One pond water sample from each line source should be obtained for fluoride determination.

Each experiment should be approximately one hour long as longer time periods might allow for larger variations in wind speed and direction. This is important since the ground level wind direction should be approximately normal to the finite line sources.

In order to verify ground level concentrations and to determine the fluoride species emitted from the ponds, it is proposed that a long path remote sensing infrared detector be placed on top of the dike. As the total path length of this instrument will be approximately 300-400 meters (pond width), accurate determination will be possible.

7.1.3 Program Costs

In order to evaluate the fluoride emissions as a function of wind velocity, it will be necessary to measure the emission rate at several



KEY:
A - Liquid Temperature Measurement
B - Upwind Ambient F_1 Sampler
C - Meteorological Tower
D - Downwind F_1 Sampler
E - Remote Infrared Sensor

Figure 7.2 Ambient and Pond Emission Sampling Network - Aerial View.

different velocities. As there will be no control over this variable, it is anticipated that approximately one month will be needed for each pond tested. Utilizing four men in the field, this will amount to about 640 man-hours field testing for each pond.

Table 7.1 gives a breakdown of the estimated costs and man-hours for a two-month field sampling program on the above basis (two ponds tested).

7.2 VERIFICATION OF THE SWIFT VAPOR-ABSORPTION SYSTEM

Several experimental approaches were considered that would allow an actual demonstration of fluoride emissions reduction upon the cooling pond. In selecting an approach, the primary criterion considered useful in demonstrating emissions reductions is the soluble fluoride level in the cooling pond waters. As shown in Figure 6.5 of this report, the correlation between pH, soluble fluorides and fluoride vapor pressure is such that one can use this parameter in judging emissions reductions.

Two approaches at demonstration are considered. The first approach involves construction of a pilot plant including acid attack system, scrubbers, evaporators, gypsum and cooling ponds. This would conveniently be done near an existing plant where small quantities of steam, electricity, and water can be obtained. The second approach would involve segregation of the gypsum and cooling ponds at an existing facility equipped with Swift vapor absorbers. After an equilibration period the soluble fluoride content of the cooling water will be measured

Table 7.1 Cost Breakdown for Fluoride Emissions Determination from Two Cooling Ponds

	Man-Hours		Cost (Direct and Indirect Labor @ 100% Overhead)
	Engineer @ $30/hr	Technician @ $20/hr	
I. Labor			
A. Presurvey	20		600
B. Planning and Administration	40		1,200
C. Equipment Preparation		40	1,200
D. Travel	15	45	1,350
E. Field Testing	325	975	29,250
F. Laboratory Analyses		100	2,000
G. Data Analysis and Report Preparation	160		4,800
Sub-total Labor			40,400
II. Non-Labor			
A. 15 Ambient Samplers @ $75 each			1,125
B. Per Diem ($30/man/day)			4,800
C. Car Rental (1,000 miles @ $.20/mile)			200
D. Communications			150
E. 2 Meteorological Towers (65') installed			3,000
F. Meteorological Equipment (10 sets)			10,000
G. Miscellaneous Equipment (F-electrodes, Thermocouples, Recorders, etc.)			1,000
H. Remote I.R. Sensor Rental			5,000
Sub-total Non-labor			25,275
III. Fixed Fee @ 8% Labor and Non-labor			5,250
IV. Total Costs			70,925

over a time period. When the fluoride content has reached a steady state value, the system will be operated in that mode (i.e., Swift scrubbers either on or off) until sufficient data has been gathered to allow conclusions to be drawn concerning operation in that mode. In the following pages each approach will be discussed at length and program costs presented.

7.2.1 Pilot Plant Approach

This study estimates that a small pilot plant, approximately one ton P_2O_5 per day, should be sufficient to obtain results for demonstration purposes. All unit-processes contained in a full-scale (500-1000 TPD) facility should be incorporated with the exception of a sulfuric acid plant. Sulfuric acid will be purchased in bulk for the experimental program. A 10,000 ft^2 cooling pond will be used to provide cooling for the barometric condenser waters. This pond will be monitored daily for fluorides. After approximately three months operation using the Swift absorbers (and producing 20 percent H_2SiF_6), the absorbers will be turned off and acid production stopped. The system will then be operated for another three month period as before. Now the pond waters should become more acidic and the fluoride levels increase. Comparison of the data from each mode will then allow conclusions to be drawn concerning the effectiveness of this system in reducing fluoride emissions.

Program costs for this approach are presented in Table 7.2 These costs were arrived at by the following methods:

- Pilot plant construction costs, sans the sulfuric acid plant, were estimated using a size exponent of 0.6 as suggested by Guthrie (1970).

Table 7.2 Pilot Plant Program Costs for the Swift Vapor Absorption System

	Quantity	Unit Cost	Total Cost
I. Plant Investment (installed 1975)			$150,000
II. Six Month Operating Costs			
Raw Materials			
Phosphate rock	550 tons	$35/ton	$ 19,250
Sulfuric acid	440 tons	$50/ton	$ 22,000
			$ 41,250
Utilities			
Electricity	720KWH/ton P_2O_5	$0.02/KWH	$ 2,640
Steam	4,000lb/ton	$0.50/M-lb	$ 370
			$ 3,020
Pilot Plant Operation			
Technician	3,120	$20/hour	$ 62,400
Engineers	520	$30/hour	$ 15,600
			$ 78,000
Laboratory Analyses			
Fluoride	Rock Samples	400 @ $7/sample	$ 2,800
	Water Samples	800 @ $5/sample	$ 4,000
pH		800 @ $3/sample	$ 2,400
			$ 9,200
Data Analyses and Interpretation			
Chemist	40	$25/hour	$ 1,000
Engineer/Scientist	80	$30/hour	$ 2,400
			$ 3,400
Reports and Project Management			
Engineer	200	$30/hour	$ 6,000
III. Miscellaneous Expenditures			
A. Travel (2 man-trips @ $250 each)			$ 500
B. Telephone			$ 100
C. Reports (60 copies @ 300 pages each)			$ 900
D. Computer			$ 500
E. Housing subsidence for on-site engineers			$ 2,000
IV. TOTAL Estimated Program Costs			$295,760

Table 7.3 Estimated Costs for Demonstration of Swift Process at a 500 TPD - P_2O_5 Facility

I. Phase 1 Costs - Plant Selection	
A. Labor (80 engineer hours @ $30/hour)	$ 2,400
B. Non-labor (travel for site selection)	$ 500
	$ 2,900
II. Phase 2 Costs - Plant Modification	
A. Engineering and supervision (200 hours)	$ 6,000
B. Non-labor (travel and communication)	$ 1,000
C. Subcontractor costs (dredging, dozing, piping, etc.)	$ 25,000
D. H_2SiF_6 storage tanks (for additional product storage one 50,000 gallon rubber-lined tank)	$ 20,000
	$ 52,000
III. Phase 3 Costs - Operation of Swift System	
A. Labor	
1) Engineering and supervision (260 hours)	$ 7,800
2) Chemist (200 hours) (F^-, P_2O_5, etc.)	$ 5,000
B. Non-labor	
1) Travel (4,000 miles @ $0.20/mile)	$ 800
2) Per diem (15 man-days @ $30/day)	$ 450
3) Communications	$ 100
	$ 12,350
IV. Phase 4 Costs - Operation without Swift System	
A. Labor	
1) Engineering (260 hours)	$ 7,800
2) Chemist (200 hours for F^-, P_2O_5, etc.)	$ 5,000
B. Non-labor	
1) Subsidy for loss of H_2SiF_6 to cooling pond (25 TPD of 100% H_2SiF_6): 75% @ $60/ton	$174,375
2) Travel (4,000 miles @ $0.20/mile)	$ 800
3) Per diem (15 man-days @ $30/day)	$ 450
4) Communications	$ 100
	$186,725
V. Phase 5 costs - Data Interpretation and Report Preparation	
A. Labor	
1) Engineer (160 hours @ $30/hour)	$ 4,800
2) Chemist (80 hours @ $25/hour)	$ 2,000
B. Non-labor	
1) Reproduction (60 copies - 300 pages @ $0.05/copy)	$ 900
	$ 7,700
Estimated Project Cost	$274,475

- Raw materials and utilities requirements were estimated using guidelines presented by Slack (1968).

As shown, total program costs are estimated to be approximately $295.760 for a six month program.

7.2.2 Conversion of Existing Facility

The other approach considered in the report for demonstrating control feasibility is as follows. An existing P_2O_5 plant, equipped with Swift vapor absorbers and currently producing fluosilicic acid will be modified by completely segregating its pond systems. This will insure that fluorine contained in the gypsum does not find its way to the cooling pond waters. The plant will then operate in two modes. In the first, fluosilicic acid will be produced 100 percent of the time the plant is in operation. At present, our best estimates indicate the Swift absorbers at most plants are not in operation at all times. This will probably require purchase of additional storage facilities to handle the additional fluosilicic acid produced during this phase of the experimental program. Assuming this additional recovered fluosilicic acid requires five day storage, one 50,000 gallon tank will be required. Once the facilities are prepared, the plant will be operated in this mode for approximately six months.

During the second operational phase of this program, the Swift absorbers will not be operated. Instead, all of the unrecovered fluorine will be condensed in the barometric condensers and go to the cooling pond. This should cause the fluorine content of the cooling waters to increase. This increase will be measured until the steady-state concentration plateau is reached. At that time the plant will be run for an additional period (approximately one month) to allow data collection and analyses. During this phase it will be necessary to subsidize the P_2O_5 company for loss of valuable H_2SiF_6. The current price of which is $60/ton on a 100 percent basis. For a 500 TPD - P_2O_5 plant, this will amount to approximately 25 TPD - H_2SiF_6 (100 percent).

Program costs for this approach are summarized in Table 7.3. The most uncertain figure in this table is that required to separate the two ponds (i.e. gypsum and cooling). For our purposes it is assumed that approximately $25,000 will be required to affect separation. However, the uncertainty in this figure is unknown but possibly large.

BIBLIOGRAPHY

Atkin, Sydney, et al., Ind. Eng. Chem., 53, 705 (1961).

Bjerrum, J.G. Schwarzenbach, and Sillen, L.G., Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances, Chem. Soc. (London), Spc. Publ. No. 7 (1958).

Brosheer, J.C.; Lenfesty, F.A.; Elmore, Kelly L., Ind. and Eng. Chem., 39, 423 (1947).

Buslaeu, V.A and Gustyakoya, M.P. Zh. Neorga. Khim. 10, 1524 (1965) In John S. Judge, J. Electrochem. Soc., 118, 1772 (1971).

Chilton, T.H. and Colburn, A.P., Ind. Eng. Chem., 26:1183 (1934).

Considine, D.M., Chemical and Process Technology Encyclopedia, McGraw-Hill Co., New York, 1974.

Crosby, N.T., J. Appl. Chem., 19, 100 (1969).

Cross, F.L. and Ross, R.W., J. Air Pollution Control Assoc., 19, No. 1.

Dahlgren, Sven-Eric, "Chemistry of Wet Process Phosphoric Acid Manufacture", Phosphoric Acid, edited by A.V. Slack, Vol I, Part I. pp. 91-156.

Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Phosphorus Derived Chemicals Segments of the Phosphate Manufacturing Point Source Category.

Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Other Non-Fertilizer Phosphate Chemicals. Segment of the Phosphate Manufacturing Point Source Category, EPA sp. EPA 440/1-75/043, Jan. 1975.

Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Basic Fertilizer Chemicals Segment of the Fertilizer Manufacturing Point Source Category, EPA, sp. EPA 440/1-73-011, Nov. 1973.

Economic Analysis of Proposed Effluent Guidelines, EPA sp. EPA 230-1-74-043, Sept. 1974.

EPA, EPA-440/1-74-006-a, Jan. 1974.

ESE, Inc., Personal Communication from J.C. Kutt to Jack Sosebee (1975).

Farrer, H.N., and Rossotti, F.J.C., J. Inorg. Nuclear Chem. 26, 1959 (1964).

Forster, J.H., "Direct Contact Evaporation", Phosphoric Acid, edited by A.V. Slack. Vol. I, Part II. pp. 579-607.

Fox, E.J., Stinson, J.M., and Tarbutton, G., Superphosphate, U.S. Dept. of Agriculture and Tenn. Valley Authority. 1964. Chapter 10. p. 237.

Getsinger, J.G., "Hemihydrate by the Foam Process", Phosphoric Acid, edited by A.V. Slack. Vol. I, Part I. p. 369.

Guthrie, K.M., "Capital and Operating Costs for 54 Chemical Programs," Chem Eng., June 14, 1979. 140-156.

Harbeck, E.G., Jr., USGS Prof. Paper 272-E, U.S. Government Printing Office, Washington D.C., 1962.

Hein, L.B., "Removal of Impurities (from Phosphoric Acid)," Phosphoric Acid, edited by A.V. Slack. Vol. I, Part II, pp. 687-708.

Huffstutler, K.K., "Pollution Problems in Phosphoric Acid Production," Phosphoric Acid, edited by A.V. Slack. Vol. I, Part II, pp. 727-737.

Inorganic Fertilizer and Phosphate Mining Industries Water Pollution and Control, EPA, 12020 FPD 09/71. Sept. 1971.

Judge, John S., J. Electrochem. Soc., 118, 1772 (1971).

Kern, Edward F., and Jones, T.R., Trans. Am. Electrochem. Soc. 49, 273 (1930).

King, W.R., and Farrell, J.K., Fluoride Emissions from Phosphoric Acid Gypsum Ponds. EPA sp. EPA 650-2-74-095, October, 1974.

Legal, C.C., and Myrick, O.D., "History and Status of Phosphoric Acid." Phosphoric Acid, edited by A.V. Slack. Vol. I, Part I. pp. 14, 32, 40.

Long, Harold, Personal communication, Feb. 1975.

Lutz, W.A., and Pratt, D.J., "Principles of Design and Operation", Phosphoric Acid, edited by A.V. Slack. Vol. I, Part I. pp. 159-212.

Mesmer, R.E., and Baes, C.F., Jr., Inorg. Chem, 8, 6(1969).

Munter, Paul A., Aepli, Otto T., Kossatz, Ruth A., Ind. and Eng. Chem., 39, 427 (1947).

Munter, Paul A., Aepli, Otto T., Kossatz, Ruth A., *Ind. and Eng. Chem.*, *41*, 1504 (1949).

Murakami, K., Hari, S., "Hemihydrate-Dihydrate Processes in Japan," *Phosphoric* Acid, edited by A.V. Slack. Vol. I, Part I. p. 287.

Pasquill, F. *Atmospheric Diffusion*, John Wiley & Sons, New York, 1974.

Sanders, M.D., "Recovery of Fluorides as By-Products," *Phosphoric Acid*, edited by A.V. Slack. Vol. I, Part II. pp. 765-778.

Schlichting, H., *Boundary Layer Theory*, McGraw-Hill, New York. (1955). Chapter 21.

Shindo, Kazuo S., Harada, Y., "NKK Process," *Phosphoric Acid*. Edited by A.V. Slack, Vol. I, Part I. pp. 328, 329.

Shireve, R.N., *Chemical Process Industries*. (16). McGraw-Hill Co., New York, 1967.

Sholtes, R.S., *et al.*, "Evaluation and Modification of Fluoride Sampling and Analytical Methods." EPA-650/2-73-007 (October, 1973).

Simons, J.H. ed., *Fluorine Chemistry*. Vols. I-III, Academic Press, New York (1954).

Slack, A.V., ed., Phosphoric Acid, Vol. I, Part I, Marcel Dekker, Inc., New York (1968).

Stumm, Werner, and Morgan, James J., *Aquatic Chemistry*. Wiley-Interscience, New York (1970).

Takeuchi, H., Tayama, I., "Mitsubishi Process," *Phosphoric Acid*, Edited by A.V. Slack, Vol. I, Part I. p. 301.

Tatera, B.S., *Parameters Which Influence Fluoride Emissions from Gypsum Ponds*. Ph.D. Dissertation, University of Florida (1970).

Teller, A.J. and Reeve, David, "Scrubbing of Gaseous Effluent." *Phosphoric Acid*, Edited by A.V. Slack, Vol. I, Part II, pp. 741-778.

Thiesenhusen, H., *Gesundh-Ing*, 53, 113-19, 1930.

Turner, D.B., *Workbook of Atmospheric Dispersion Estimates*, U.S. Public Health Service Publication, No. 999-AP-26, May 1970.

U.S. Department of Health, Education and Welfare, *Atmospheric Emissions from Wet-Process Phosphoric Acid Manufacture*, National Air Pollution Control Administration, Raleigh, N.C. (1970).

Yasuda, T., Miyamoto, M., "Nissan Process." *Phosphoric Acid*. Edited by A.V. Slack, Vol. I, Part I. pp. 307, 309.